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Binary systems based on aromatic amines with a view of development of novel hardeners for epoxy resins

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Abstract
Three binary systems based on aromatic amines [4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS), 4,4′-diaminodiphenyl ether (DDE) and *m*-phenylenediamine (MPDA)] were investigated by differential scanning calorimetry (DSC). Phase diagrams for different compositions were constructed. The DSC results showed that all binary systems form simple eutectic mixtures. Formation of eutectic physical mixture of MPDA–DDM and MPDA–DDS was confirmed by powder XRD study. In the case of DDE–DDS system, it was found that besides the eutectic mixture a small amount of the charge transfer complex forms with the novel crystal structure.

Keywords Aromatic amine · Phase diagram · DSC · Eutectic melting

Introduction

Development of new high-performance materials is one of the major challenges today. Because of their excellent properties such as thermal stability, strength, chemical resistance, very high adhesive properties, epoxy thermosetting materials are widely used as adhesives, coatings, compounds and matrices for composite materials [1, 2].

Depending on the type of curing agent and the curing conditions, it is possible to obtain materials with various mechanical properties and thermal stability and heat resistance. Curing agents such as diamines and anhydrides are useful in most of the important applications of epoxy resins. The use of anhydride hardeners in such compositions gives the materials with high physical and mechanical properties [3]. Aromatic diamines, being used as curing agents, increase thermal and chemical resistance of the cured epoxy resin in comparison with the aliphatic diamines [4, 5], which allow to use epoxy/aromatic amine systems as matrices in high-performance fiber composites for aerospace applications.

Epoxy formulations based on aromatic amines such as 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl sulfone (DDS), *m*-phenylenediamine (MPDA) and *p*-phenylenediamine (PPDA) have been studied for decades [6–13]. However, high melting temperatures as well as low solubility in epoxides are still the main drawback of most of aromatic amines. Also there are some recent works focused on synthesis of novel aromatic amine curing agents [14–18]. Unfortunately, the significant reduction of curing temperature and improving of thermal properties of polymers has not been reached.

In the 1960s, there were several interesting attempts in development of hardeners based on eutectic mixtures of two or three aromatic amines [19–21]. However, only two mixtures (including MPDA–DDM) were suggested for commercial application without detailed and adequate substantiation of their composition. Thereafter, this idea has not received further expansion. Therefore, the aim of this study was the investigation of binary systems based on aromatic amines with attempt to develop eutectic mixtures capable to decrease curing temperature and improve heat resistance of obtained polymer materials.

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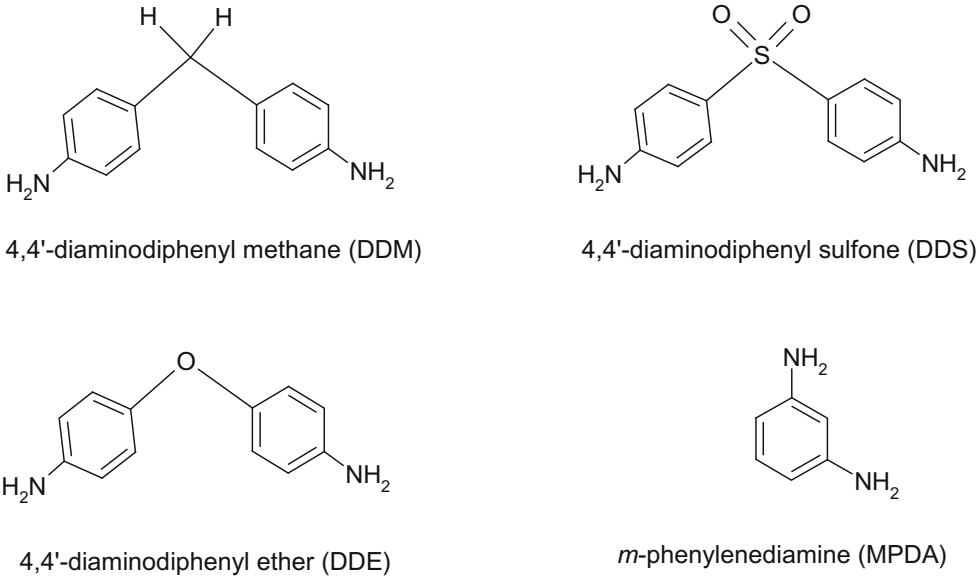
Fig. 1 Chemical structures of used aromatic amines



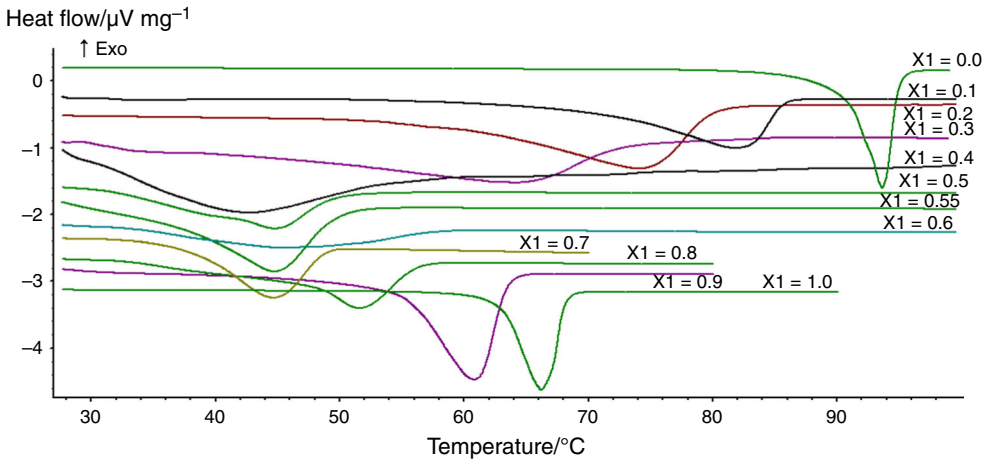


Fig. 2 DSC curves of MPDA (1)–DDM (2) system

It is well known that differential scanning calorimetry (DSC) is an effective and sensitive method widely used for the characterization of any kind of phase transitions [22–27]. A number of binary mixtures with aromatic amines (like diphenylamine, *o*-phenylenediamine and aniline) were studied with a view of developing energetic materials' stabilizers and materials for various electronic and optoelectronic applications [28–30].

In this work, three systems (MPDA–DDM, MPDA–DDS and DDE–DDS) have been investigated and phase diagrams have been studied using DSC technique. The crystal structures of parent amines and their eutectic mixtures were qualitatively investigated using powder X-ray diffraction (XRD).

Table 1 Experimental solid + liquid equilibrium temperatures for the MPDA (1)–DDM (2) system

*X*1	T_{fus1}/°C	T_{fus2}/°C
0.00	90.9	
0.10	69.9	
0.20	59.5	
0.30	39.1	
0.40	25.7[a]	
0.50		31.2
0.60		33.2
0.70		37.6
0.80		47.5
0.90		55.1
1.00		62.9

[a]Related to eutectic mixture

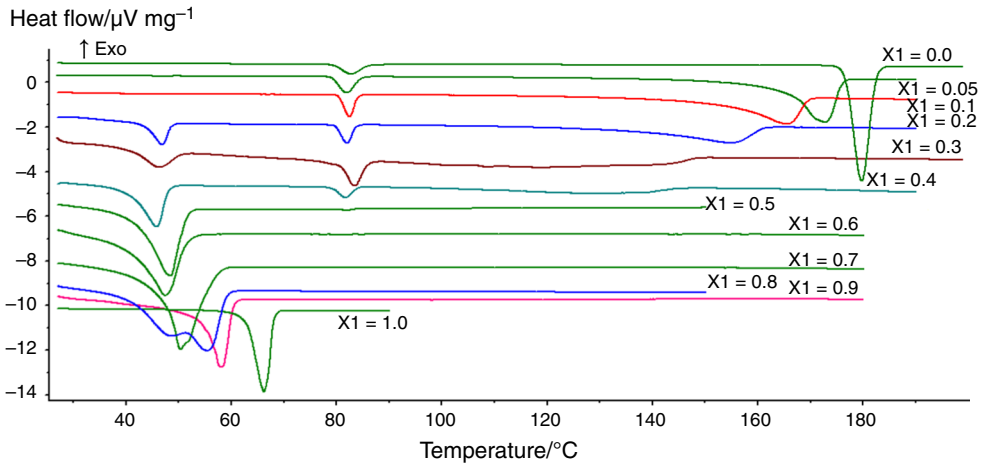


Fig. 3 DSC curves of MPDA (1) –DDS (2) system

Table 2 Experimental solid + liquid equilibrium temperatures for the MPDA (1) –DDS (2) system

*X*1	T_{fus1}/°C	T_{fus2}/°C
0.00	177.1	
0.05	167.6	
0.10	160.4	
0.20	138.4	
0.30	93.4	
0.40	39.2[a]	
0.50		42.1
0.60		42.7
0.70		47.6
0.80		51.4
0.90		54.7
1.00		62.9

[a]Related to eutectic mixture

Experimental

Materials

m-Phenylenediamine (MPDA), 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl ether (DDE) and 4,4′-diaminodiphenyl sulfone (DDS) were obtained from Fluka and were used without further purification. Chemical structure of MPDA, DDM, DDE and DDS is shown in Fig. 1.

Methods

The binary mixtures were slowly heated on aluminum plate up to the temperature of highest melting component. After crystallization mixture was mulled, the sample melting was investigated with a Netzsch DSC 214 Polyma differential scanning calorimeter. The measurements were made under nitrogen atmosphere with constant heating rate of 5 K/min. Phase diagrams were established in melting temperature *vs* composition.

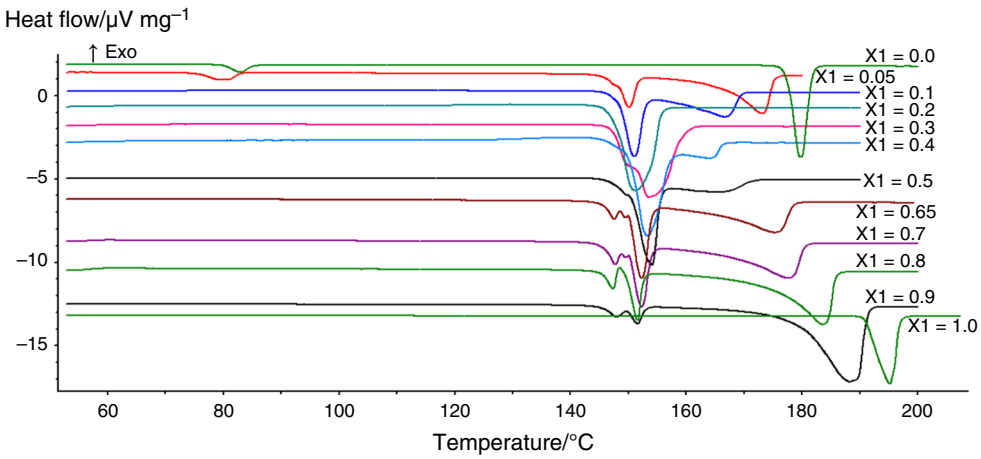


Fig. 4 DSC curves of DDE (1)–DDS (2) system

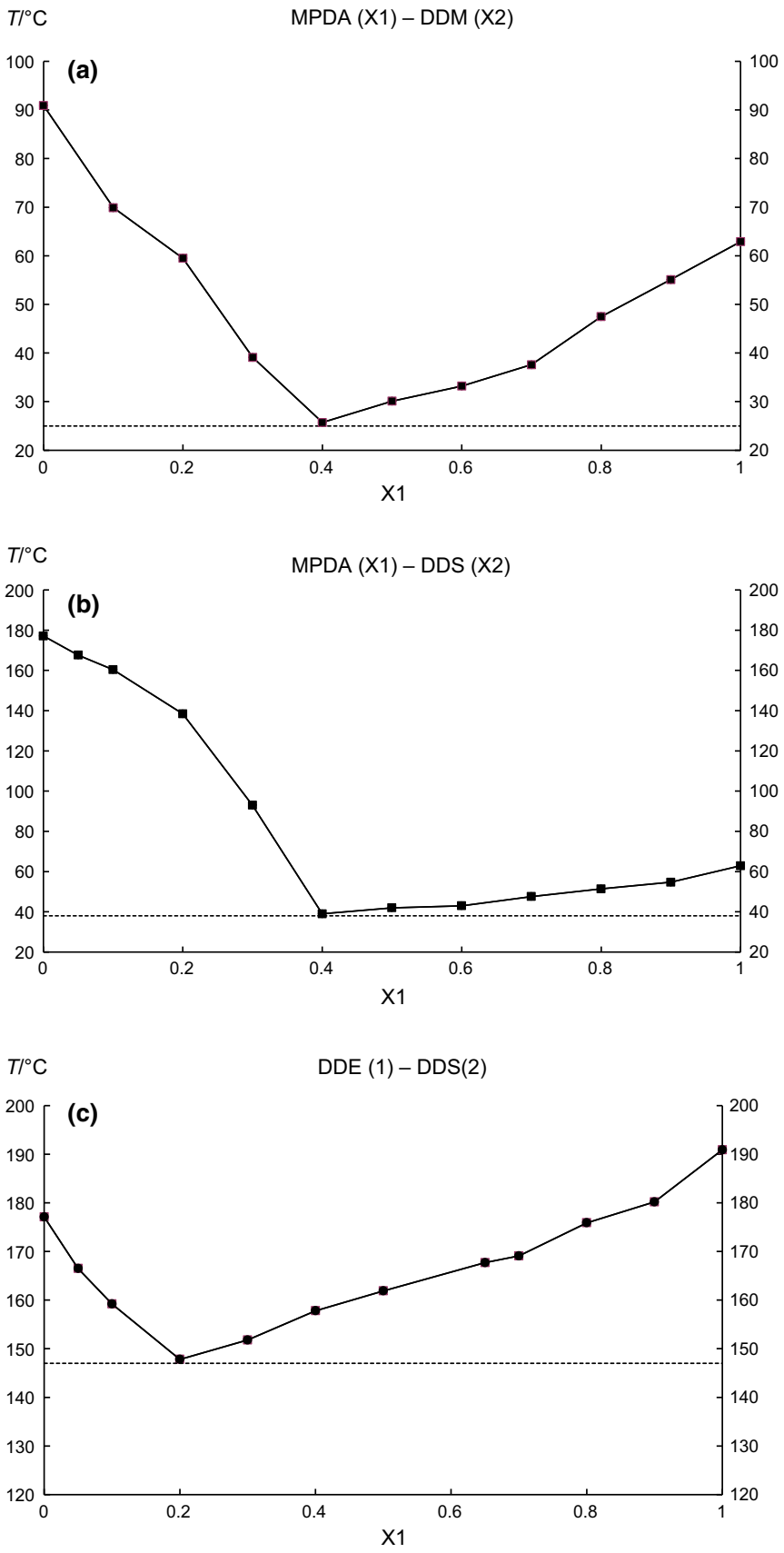


Fig. 5 Phase diagrams of investigated systems: MPDA–DDM (**a**), MPDA–DDS (**b**), DDE–DDS (**c**)

Table 3 Experimental solid + liquid equilibrium temperatures for the DDE (1)–DDS (2) system

$X1$	T_{fus1}/°C	T_{fus2}/°C
0.00	177.1	
0.05	166.5	
0.10	159.2	
0.20	147.8[a]	
0.30		151.8
0.40		157.8
0.50		161.9
0.65		167.7
0.70		169.1
0.80		175.9
0.90		180.2
1.00		190.9

[a]Related to eutectic mixture

Structures of eutectic mixtures were confirmed by powder XRD using Rigaku MiniFlex 600 diffractometer equipped with a D/teX Ultra detector. In this experiment, Cu Kα radiation (30 kV, 10 mA) was used, and $K\beta$ radiation was eliminated with Ni filter. The diffractograms were determined at room temperature in the reflection mode, with scanning speed of 5° min^{-1}. Samples were loaded into a glass holder. Patterns were recorded in the 2θ range between 3° and 45° without sample rotation.

Results and discussion

As was mentioned above, the MPDA–DDM mixture is commercially available, but there is no information in the literature on studying the phase diagram of this system. Herewith, it is assumed that the MPDA–DDM = 40–60 composition is a eutectic mixture [19]. The DSC curves of MPDA–DDM system are shown in Fig. 2. The experimental solid–liquid equilibrium temperatures for the different ratios are given in Table 1.

The melting peak on DSC curve of the composition corresponding to the eutectic mixture is sufficiently broadened since obtaining the crystalline sample was difficult because of the low melting point of the mixture.

Next, the system MPDA–DDS was investigated (Fig. 3). The experimental solid–liquid equilibrium temperatures for the different ratios of that system are given in Table 2.

As seen, in both systems the eutectic mixture has a composition $X1 = 0.4$.

Of special interest is the study of DDE–DDS system, since each of these aromatic amines allows to obtain materials with high heat resistance. However, melting of pure DDE and DDS occurs at high temperatures. It is interesting to note that during the mastication of pure amines electrostatic repulsion of the particles was observed (Figs. 4 and 5; Table 3).

The phase diagrams were constructed based on the data obtained for the appropriate systems.

Powder X-ray diffraction studies were performed to investigate structures of amine mixtures in comparison

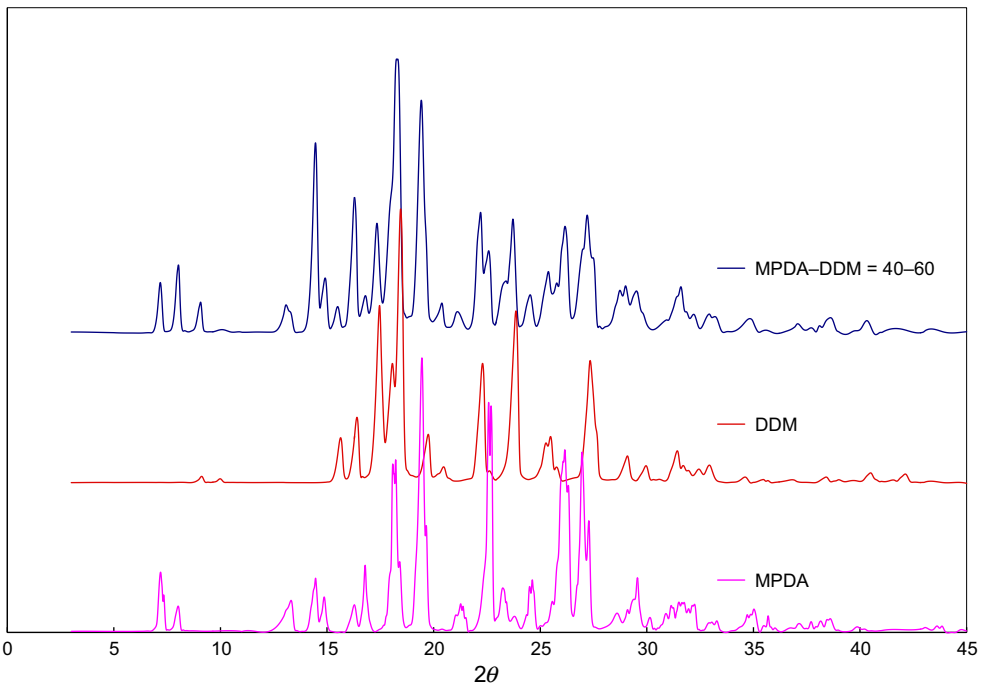


Fig. 6 Powder X-ray diffraction pattern of MPDA, DDM and eutectic mixture

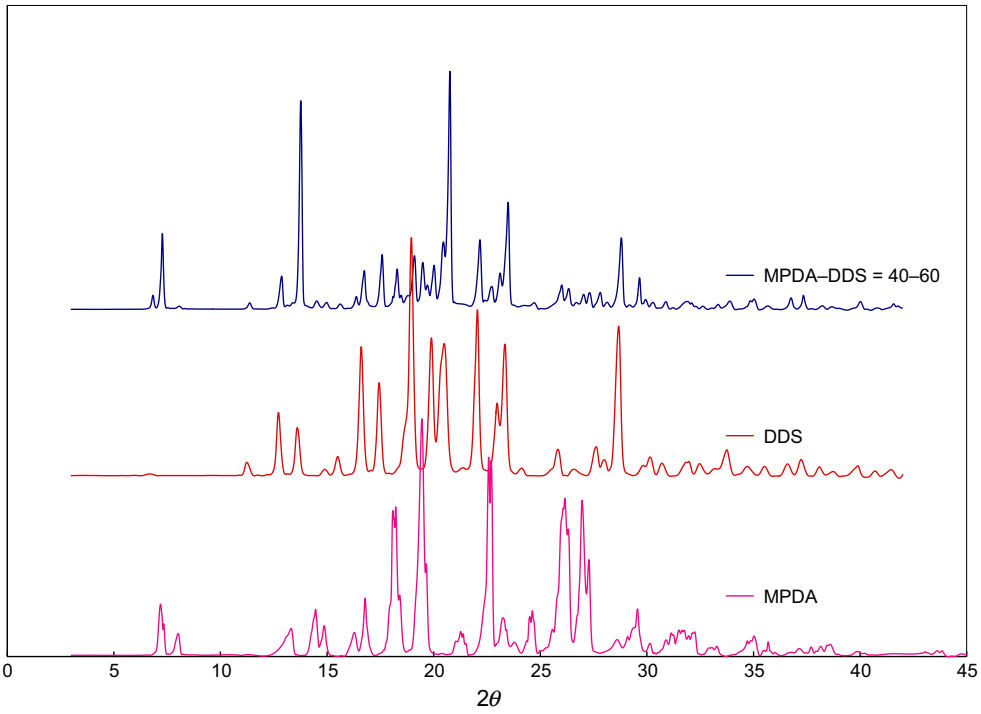


Fig. 7 Powder X-ray diffraction pattern of MPDA, DDS and eutectic mixture

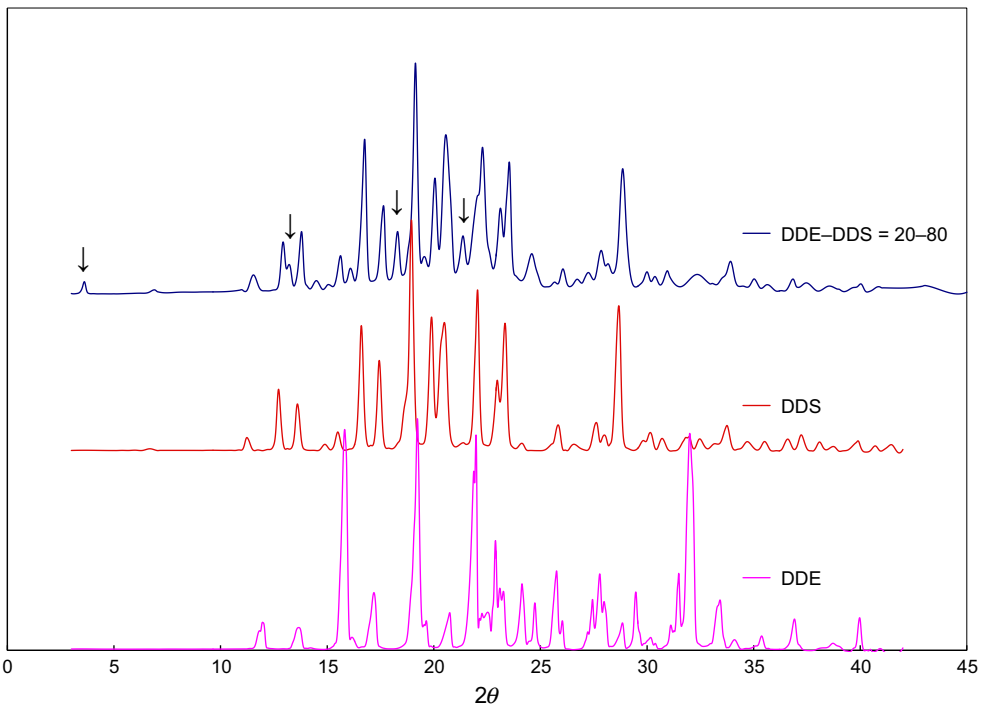


Fig. 8 Powder X-ray diffraction pattern of DDE, DDS and their eutectic 20–80 mixture. Unique peaks of the complex formed are shown with arrows

with those of the pure components. The powder XRD pattern of MPDA, DDM and their eutectic mixture is given in Fig. 6.

As can be seen, diffraction pattern of the eutectic mixture MPDA–DDM = 40–60 (Fig. 6) contains both of the components' peaks and can be regarded as a summary pattern. While as mixture diffraction pattern does not contain its own unique peaks, MPDA–DDM = 40–60 represents a physical mixture of the initial amines. In case of MPDA–DDS = 40–60 system, a similar picture is observed (Fig. 7).

As to the last system, in the PXRD pattern of DDE–DDS = 20–80 (Fig. 8) several new peaks were detected which cannot be associated with parent components.

Thus, besides the signals of eutectic mixture of DDE–DDS, several new peaks which can indicate the formation of the complex were observed. It is important to note that the peak at the low 2θ area near 3° is absent on patterns of pure DDE and DDS, so it can show formation of the larger unit cell with bigger lattice constant. Probably DDE and DDS form mostly a eutectic mixture as well as some amount of a charge transfer complex, which explains the electrostatic repulsion of particles. Thereby, for any ratio of DDE and DDS such complex can be formed in small amounts, but just at a DDE–DDS = 20–80 ratio the equilibrium is shifted toward its priority formation. The formation of such complex can influence on epoxy oligomers curing process; therefore, the further study of this system is of great interest.

Conclusions

A series of binary systems of aromatic amines were investigated by DSC method, which allowed to obtain the compositions of eutectic mixtures. Phase diagrams for all systems were plotted. DSC showed that *m*-phenylenediamine forms with 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenyl sulfone single eutectic mixtures with diamine compositions: $x_{eu} = 0.4$ in both cases. In the other side, study of the 4,4′-diaminodiphenyl ether–4,4′-diaminodiphenyl sulfone system showed that DDE–DDO at ratio 20–80 forms an eutectic mixture as well as some amount of complex with different crystal structure. The obtained result allows the use of such eutectic mixtures as hardeners of epoxy oligomers. A significant reduction in the melting temperature of the curing agent will considerably simplify its dissolution and homogeneous distribution in the resin. The study of the formed DDE–DDS complex effect on the curing of epoxy compositions will be also of interest.

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