Glass-fibre reinforced composite materials based on unsaturated polyester resins

Zoltán Budai · Zsolt Sulyok · Viktória Vargha

Abstract The effect of glass-fibre content on the thermal and mechanical properties of cross-linked composites based on unsaturated polyester resins have been investigated by thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical thermal analysis and by measuring the heat distortion temperature (HDT). Two different matrix resins and two different glass mats were used, and the glass-fibre contents varied. Altogether 12 composite systems were tested. The glass- transition temperature of each composite was characteristic to the matrix resin and did not depend on the glass-fibre content, as it was expected. The effect of glass-fibre content on the storage modulus and on HDT has been elucidated. It has been found that up to 12 mass% (6 vol%) glass-fibre content the HDT did not change, above this value it increased with increasing glass-fibre content for each composite, but not at the same extent. This means that matrix-fibre interaction has an important role in the performance of the composites at elevated temperatures. Storage moduli increased with increasing glass-fibre content. The temperatures detected by dynamic mechanical thermal analysis corresponding to the storage modulus of 750 MPa—calculated by Takemori—are above the glass-transition and also increased with higher glass-fibre content in accordance with the real heat-distortion temperature measurements. It may be concluded that the effect of reinforcement on the performance of the composite could be detected more reliably by HDT measurements, since it gives information on the deformation of the composites. Matrix-fibre interaction has an essential role on the performance and on the HDT of the composite materials.

Keywords Glass-fibre reinforced composites · Unsaturated polyesters · Heat distortion temperature · HDT · Thermogravimetry · Differential scanning calorimetry · Dynamic mechanical thermal analysis

Introduction

Composites and their characterisation

In spite of the fact that glass-fibre reinforced composite materials based on unsaturated polyester resins have been used for very long time [1] their market and versatile application has still been expanding [2, 3]. Chemistry of polyester formation has been discussed in monographs [4, 5]. There is a great number of processing technics for these composite materials including lamination, compression moulding, filament winding, rotational casting, pultrusion etc. [1, 6, 7]. Similarly to all thermosetting systems they cross-link in the mould after processing, the cross-linked material does not soften anymore and is non-soluble. Many authors dealt with the analysis of curing of unsaturated polyester resins [8, 9]. The behaviour of thermosetting systems before, during and after processing is well demonstrated by their Time-Temperature-Transformation (TTT) diagram, which represents the iso-conversion curves showing relation between the time of curing and temperature of curing. A comprehensive TTT-diagram for an unsaturated polyester resin was determined and constructed by Ramis and Salla [10] (Fig. 1).

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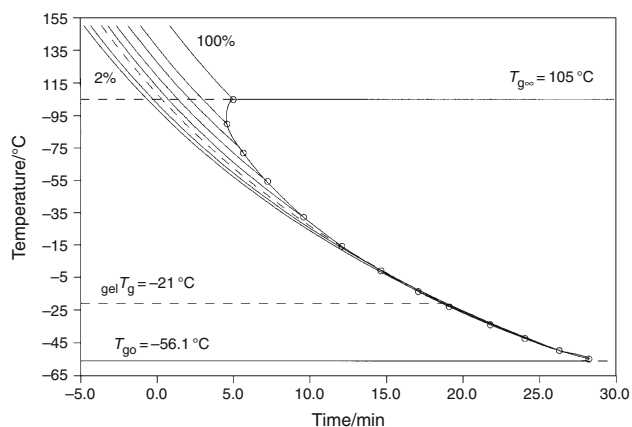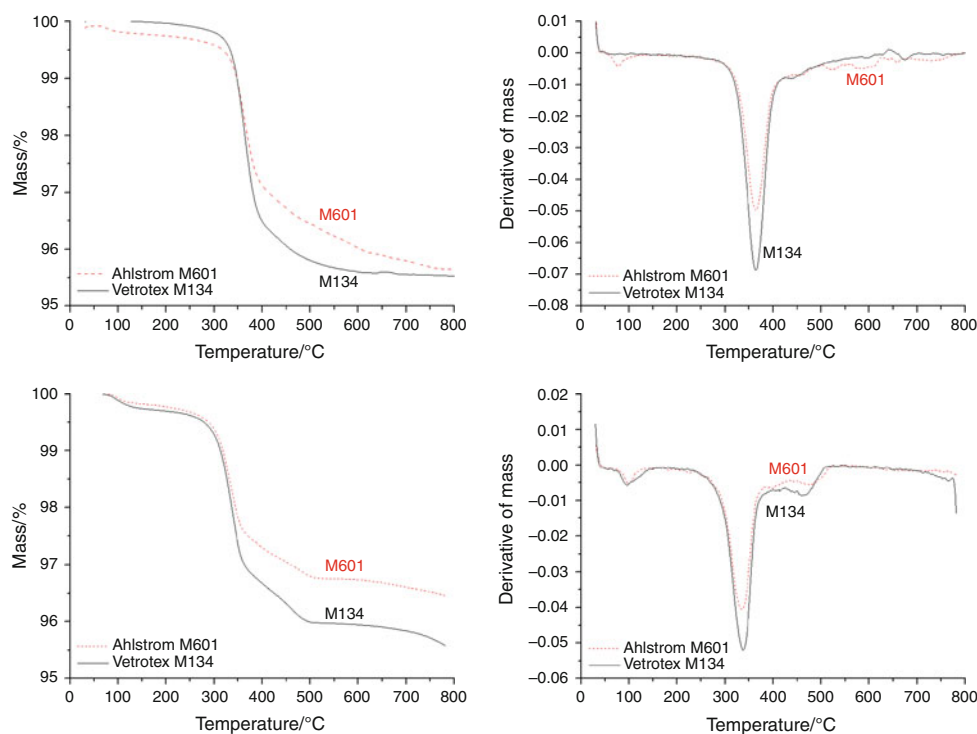e-mail: vvargha@mail.bme.hu

Fig. 1 Time-Temperature-Transformation diagram of an unsaturated polyester resin [10] (Gelation curve and iso-conversion curves at 2, 10, 45, 80, 90, 95, 98 and 100% conversions)

Trends of composite development

Composites are multiphase systems including the matrix resin and the reinforcing material. They exhibit outstanding mechanical performance together with low density. Their properties can be tailored by properly selecting the matrix resin, the reinforcing material and their ratio, during which the interphasial interactions play the essential role. A new and exciting field of research represent the composites based on liquid crystalline polymers or reinforcements. Polymeric liquid crystals comprise the advantageous properties of polymers and of liquid crystals [11, 12]. Polymer coated coextruded optical fibres of high

mechanical strength and of low thermal expansion has been prepared [13]. Liquid crystalline polyesters have been used for laminating flexible insulating sheets for electric circuits and heat resistant insulating sheets [14]. Liquid crystalline polymers have also been applied for in situ synthesized self-reinforcing composites [15, 16]. Poly(ethylene 2,6-naphthalate) (PEN) and poly(ethylene terephthalate) (PET) composite fibres reinforced with a thermotropic liquid crystal polymer (TLCP) were prepared by the melt blending and spinning process to achieve high performance fibres with improved processability [17]. Liquid crystalline polyesterimides can be promising candidates as novel base film materials in flexible printed circuit boards (FPC) [18]. Research and utilisation of nanocomposites have been extensively developing during the past years [19].

Heat distortion temperature

One of the most important characteristics of composite materials is their mechanical performance under load at high temperatures. This may be characterised by their heat distortion (deflection) temperature (HDT), i.e. the temperature at which the sample specimen under a specific load attains a certain deformation as described in ASTM D-648-72, MSZ 13002-85, DIN 53641 and ISO 75. This temperature is one of the most important property for selecting a composite material for design engineering and manufacture of products.

The HDT can be basically correlated with the glass-transition temperature of the matrix polymer. The effect of

Fig. 2 TG thermograms of the pure glass mats in purging nitrogen (up) and oxygen (down)

Table 1 Results of thermogravimetric analysis of the pure glass mats

	Ahlstrom M601			Vetrotex M 134		
	Onset of decomposition		Residue	Onset of decomposition		Residue
	T_{onset}/°C	m_{onset}/mass%	mass%	T_{onset}/°C	m_{onset}/mass%	mass%
Nitrogen	334	99.7	95.7	334	99.9	95.5
Oxygen	300	99.7	96.5	300	99.6	95.6

T_{onset} onset temperature of the decomposition of the finishing material

m_{onset} mass at T_{onset}

the type and quantity of the reinforcing material on HDT is essential, since deformation of the composite under given conditions determines its performance.

Sepe briefly reviews the HDT test as defined in the ASTM Test Method for Deflection Temperature of Plastics under Flexural Load (D648) and the International Standards counterpart, ISO 75. It will then be discussed an alternative method for capturing a more complete picture of the effect, that temperature has on modulus. This technique, known as dynamic mechanical analysis (DMA) provides an excellent tool for evaluating materials and comparing their mechanical performance over a wide range of temperatures [20]. This method reveals the viscoelastic feature of polymers [21–23]. Additives improving the blending properties of matrix polymers may also result in the increase in HDT [24, 25].

Similar to HDT is the Vicat softening temperature described in ASTM D1525 and ISO 306. This method gives similar results but suitable for homogeneous materials or plastics of fine multiphase structure.

Takemori established the relationship between modulus and HDT [26, 27]. Under flexural loading (three-point bending), the deflection of an ideal beam is given by

$$\eth = \frac{FL^3}{48EI} = \frac{\eth_{max}L^2}{6Eh} = \frac{\varepsilon_{max}L^2}{6h} \tag{1}$$

where δ = deflection, L = distance between supports, h = specimen width, F = applied load, I = areal moment of inertia of a beam, σ_{max} = maximum fibre stress, ε_{max} = maximum fibre strain, E = modulus of sample. ASTM D648-72 test specifies a maximum fibre stress of 455 or 1820 kPa for engineering polymers. In HDT test several contributions to the total deflection must be considered. Equation 1 gives the ideal small strain elastic deflection. Since the sample is initially loaded at $T_0 = 23$ °C, there is an initial deflection $\delta(T_0)$ which must be subtracted to yield the net elastic deflection.

$$\eth_{elastic}(T) = \eth(T) - \eth(T_0) = \frac{FL^3}{48I}\left[\frac{1}{E(T)} - \frac{1}{E(T_0)}\right] \tag{2}$$

Further on, the contribution due to creep must also be considered.

$$\eth_{creep} = \dot{\varepsilon}_{creep}\Delta t\left(\frac{L^2}{6h}\right) \tag{3}$$

where $\dot{\varepsilon}_{creep}\Delta t$ is the strain due to creep during a time interval Δt (see Eq. 1).

The effect of thermal expansion resulting in a negative deflection, since the bottom supports are rigidly fixed, can be given as:

$$\eth_{thermal} = -\alpha h\Delta T \tag{4}$$

where α = the thermal expansion coefficient.

All of these contributions to deflection must be incorporated into the time–temperature profile of the HDT test, i.e. a heating rate of 2 °C min^{-1}. Thus, the total deflection at temperature T is given by:

$$\begin{aligned}
\eth_{net}(T) &= \int_0^t \left\{\dot{\delta}_{elastic}^i + \dot{\delta}_{creep}^i + \dot{\delta}_{thermal}^i\right\}\mathrm{d}t \\
&= \frac{FL^3}{48I}\left\{\frac{1}{E(T)} - \frac{1}{E(T_0)}\right\} + \int_0^t \left(\frac{L^2}{6h}\right)\dot{\varepsilon}_{creep}^i\mathrm{d}t \\
&\quad - \int_{T_0}^T \alpha_i h\mathrm{d}T
\end{aligned} \tag{5}$$

where t is the elapsed time when the system reaches temperature T.

The contributions due to creep and thermal expansion become significant only at high temperatures and consequently long test times. Since these two contributions are of opposite signs and tend to eliminate each other, the problem may be simplified by neglecting the effect of creep and thermal expansion enabling a good qualitative understanding the relation of HDT and modulus-temperature properties.

By neglecting creep and thermal expansion Eq. 5 simplifies:

$$\eth_{net}(T) = \frac{FL^3}{48I}\left\{\frac{1}{E(T)} - \frac{1}{E(T_0)}\right\} \tag{6}$$

By rearranging Eq. 6 and solving it for the tensile modulus E_{10} which will produce a net deflection of 0.25 mm will result:

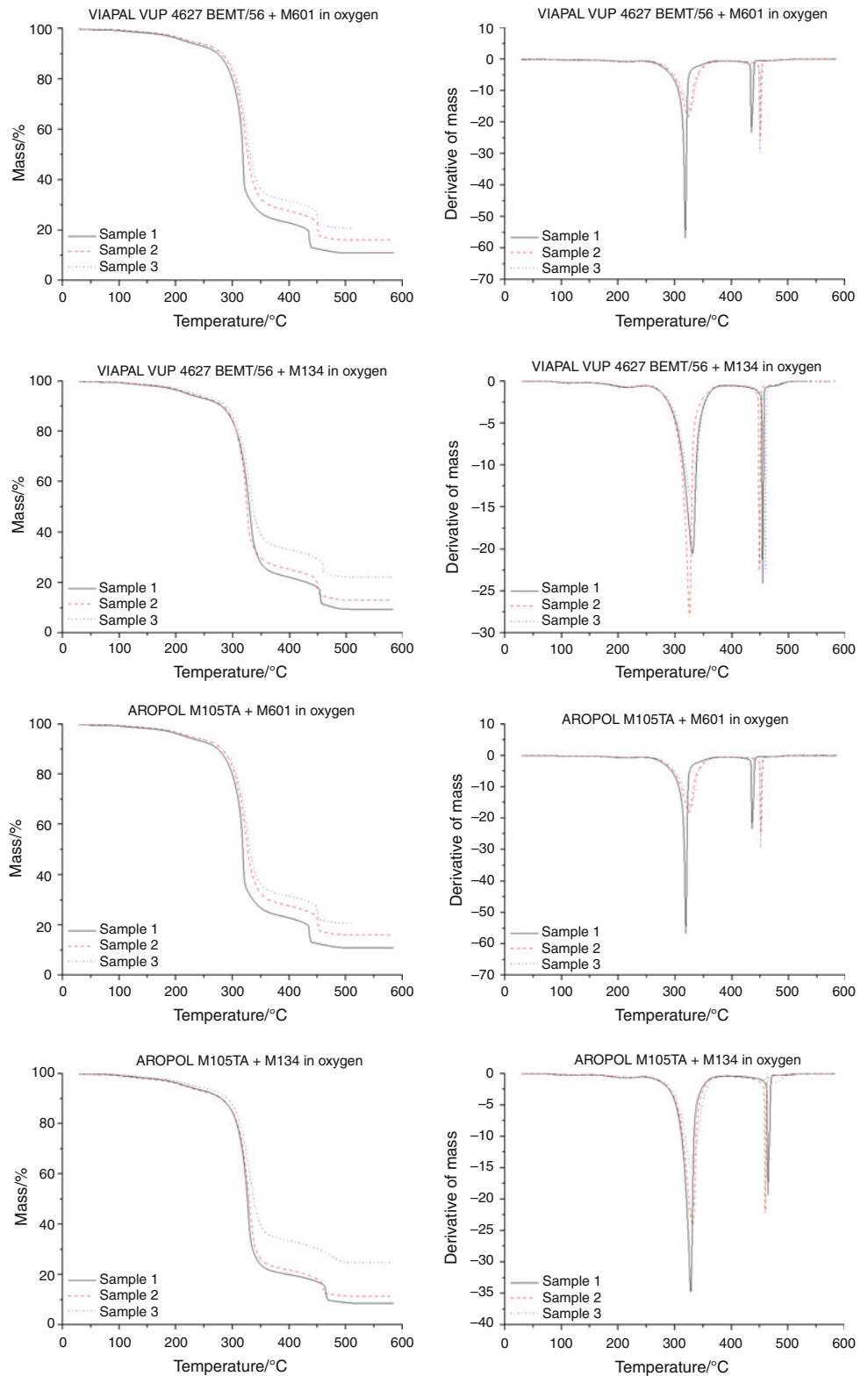**Fig. 3** TG thermograms of the composites in purging nitrogen
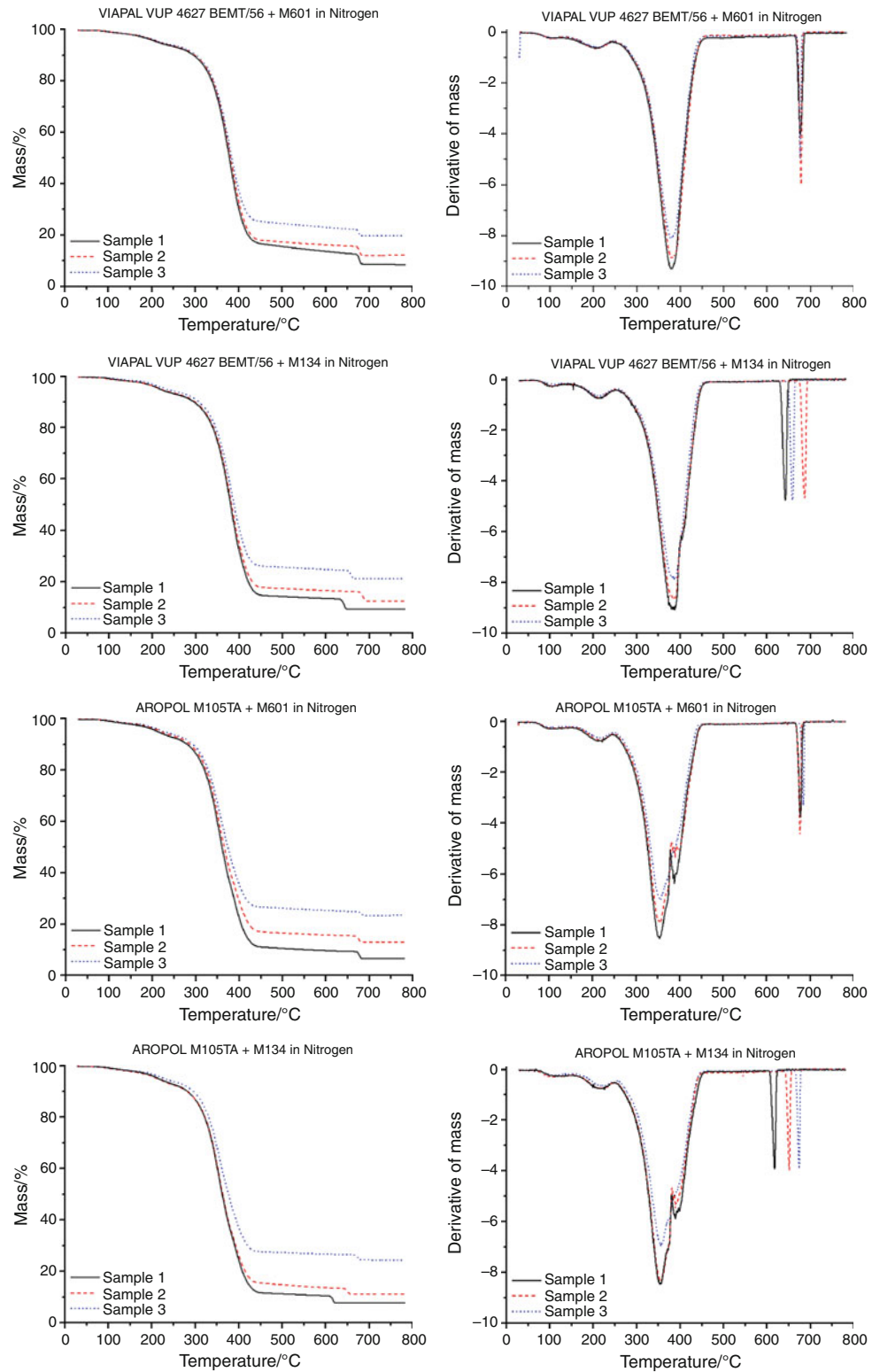
$$E_{10} = \frac{FL^3}{48I}\left\{\frac{1}{0.25\,\text{mm} + \delta(T_0)}\right\} \qquad (7)$$

where $\delta(T_0)$ is the initial deflection shown in Eq. 2. $\delta(T_0)$

is about 0.075 mm which corresponds to a modulus of 3.24 GPa at 23 °C. Thus, by using a standard ASTM HDT specimen bar at a maximum fibre stress of 1.82 MPa

Fig. 4 TG thermograms of the composites in purging oxygen

$$E_{10} \sim 0.75 \text{ GPa} \qquad (8)$$

This means that by assuming negligible creep and thermal expansion the specimen will deflect 0.25 mm under the applied load F of 1.82 MPa when the tensile modulus of the

sample has fallen to E_{10} during heating at 2 °C min^{-1}. The corresponding temperature is the HDT. So HDT can be predicted from the modulus-temperature curve.

The aim of our experiments was the elucidation of the effect of glass-fibre content on the HDT of the composites based on

Table 2 Results of thermogravimetric analysis of the composites in purging nitrogen

Glass-fibre content	Main step of decomposition		Derivative of the main decomposition step				Residue
			Peak onset		Peak minimum		
mass%	T_{onset}/°C	m_{onset}/mass%	T/°C	m/mass%	T/°C	m/mass%	mass%
VIAPAL VUP4627 BEMT/56							
M 601 14	334	90	245	94	380	53	13
19	334	90	245	94	51	16	17
24	334	90	245	94	48	22	28
M 134 14	331	90	251	96	385	52	13
17	331	90	251	96	47	16	15
26	331	90	251	96	44	25	29
AROPOL M105 TA							
M 601 10	313	90	245	94	355	64	9
17	313	90	245	94	355	59	15
28	313	90	245	94	355	55	25
M 134 13	312	90	245	94	355	65	11
15	312	90	245	94	355	57	13
29	312	90	245	94	355	56	27

T_{onset} onset temperature of thermal decomposition

m_{onset} mass at T_{onset}

unsaturated polyester resins, and revealing the relation between the measured HDT and the temperature detected by dynamic mechanical analysis attained at the modulus corresponding to 750 MPa. For attaining comprehensive results two different matrix resins and two different glass mats have been used, each of them has been prepared with three different glass-fibre content, i.e. 12 different composites have been tested.

Experimental

Materials

Unsaturated polyester resin matrix: Viapal VUP 4627 BEMT/ 56 (Vianova) and AROPOL M105 TA (Ashland Finland Oy). Redox initiator system was used, in which the activator is a soap of multivalent metal, dissolved in the resin. The initiator was Butanox® M-50 (33 wt% methyl-ethyl-keton-peroxide in dimethyl phthalate, AKZO NOBEL). 2 vol% Butanox® M-50 was applied based on resin.

Glass mat: Vetrotex M134 (Saint-Gobain Vetrotex Reinforcement GmbH); glass-fibre chopped strand mat made from E-glass, surface-treated (300 g m^{-2}), and Ahlstrom M601 (Ahlstrom Corporation); Glass-fibre chopped strand mat made from E-glass, surface-treated (300 g m^{-2}).

Preparation of the composites

The composites have been prepared by hand lamination in the form of a disc using different number of glass mat layers,

namely 4, 6 and 11 layers, thus ensuring the different glass-fibre content. The diameter of the thin-walled round form made of stainless steel was 255 mm, its height 12 mm ensuring enough thickness of the discs for the test specimen. The form was kept in thermostat at 25 °C to avoid stresses during polymerisation cross-linking. Both matrix resins were prepared with the two glass mats at three different glass-fibre content, meaning that altogether 12 different composite discs with diameter of 235 mm and thickness of 10 mm were prepared after final turning. Test specimen for HDT, DSC and DMA measurements have been machine cut from these composite discs.

Methods and equipment

Thermogravimetric analysis (TG)

The measurements took place between 30 and 700 °C in purging nitrogen (40 mL min^{-1}) and between 30–550 °C in purging oxygen (40 mL min^{-1}) at a heating rate of 10 °C min^{-1} by using a Perkin Elmer TG 6. The samples for TG and DSC measurements were the homogenized chip gained from a test specimen for HDT measurements by cutting perpendicularly to the glass mat in the specimen. 10 mg sample was weighed in for each TG analysis.

Heat distortion temperature (HDT)

Test specimen for HDT measurements have been milled from the prepared composite discs in the following: the

Table 3 Results of thermogravimetric analysis of the composites in purging oxygen

	Glass-fibre content	Main step of decomposition		Derivative of the main decomposition step				Residue
				Peak onset		Peak minimum		
	mass%	T_{onset}/°C	m_{onset}/mass%	T/°C	m/mass%	T/°C	m/mass%	mass%
VIAPAL VUP4627 BEMT/56								
M 601	14	300	91	252	93	320	49	11
	19	300	91	252	93	325	54	16
	24	300	91	252	93	330	56	21
M 134	14	305	90	250	93	330	48	9
	17	305	90	250	93	325	50	13
	26	305	90	250	93	330	58	22
AROPOL M105 TA								
M 601	10	306	90	252	93	325	45	7
	17	306	90	252	93	330	54	14
	28	306	90	252	93	320	63	24
M 134	13	305	90	250	93	330	43	9
	15	305	90	250	93	330	45	11
	29	305	90	250	93	330	61	25

T_{onset} onset temperature of thermo-oxydative decomposition

m_{onset} mass at T_{onset}

composite discs have been cut to specimen of 8 × 130 × 10 mm, then ground on a special grinding pad to the size of 9 × 6×127 mm ± 0.01 mm. The glass mat layers were parallel to the side of 127 mm.

The measurements took place according to the standards MSZ 13002-85, DIN 53641, ASTM D 648-72, ISO 75 in the temperature range of 25–195 °C applying a three-point-bending stress of 1.8 MPa (123 + 341 g loading mass) at a heating rate of 2 °C min^{-1}. The size of the test specimen was 9 × 6 × 127 mm; CEAST 6510/517 equipment was used. The number of parallel measurements was at least 3.

Differential scanning calorimetry (DSC)

A Perkin Elmer DSC 7 was used from −60 to 230 °C at a heating rate of 10 °C min^{-1} in purging nitrogen of 40 mL min^{-1}. 4–5 mg sample chip was weighed in a closed aluminium pen.

Dynamic mechanical analysis (DMA)

A Perkin Elmer DMA 7 was used in the temperature range of 30–200 °C at a heating rate of 3 °C min^{-1} according to ASTM D 4065-94. Type of load was single cantilever

Table 4 Glass-fibre content of the composites determined by thermogravimetry

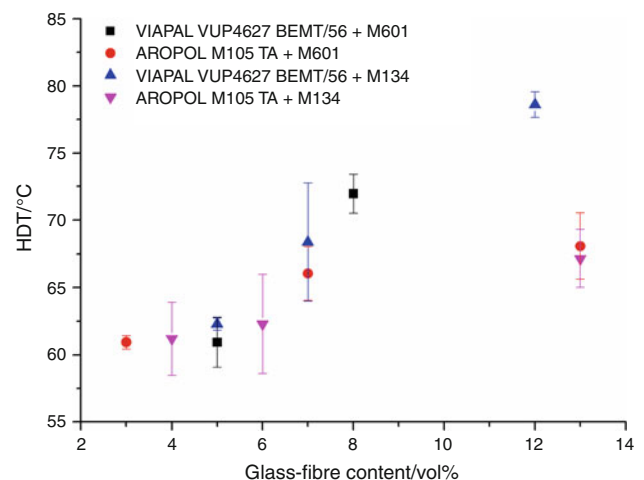| Matrix	VIAPAL VUP4627 BEMT/56			AROPOL M105 TA		
Glass mat	Sample no.	Glass-fibre content		Sample no.	Glass-fibre content	
		mass%	vol%		mass%	vol%
Ahlstrom M601	1	11	5	1	7	3
	2	17	8	2	15	7
	3	22	11	3	25	13
Vetrotex M 134	1	10	5	1	9	4
	2	14	7	2	12	6
	3	23	12	3	26	13

Fig. 5 Relation between the glass-fibre content and heat-distortion temperature of the composites

Table 5 HDT values of the composites with different glass-fibre content

Matrix	VIAPAL VUP4627 BEMT/56					AROPOL M105 TA				
Glass-mat	Sample no.	Glass-fibre content		HDT/°C		Sample no.	Glass-fibre content		HDT/°C	
		mass%	vol%	Average	St.dev.		mass%	vol%	Average	St.dev.
Ahlstrom	1	11	5	60.9	±1.9	1	7	3	60.9	±0.5
M 601	2	17	8	72.0	±1.5	2	15	7	66.1	±2.0
	3	22	11	>95[a]	n.a.	3	25	13	68.1	±2.5
Vetrotex	1	10	5	62.3	±0.5	1	9	4	61.2	±2.7
M 134	2	14	7	68.4	±4.4	2	12	6	62.3	±3.7
	3	23	12	78.6	±1.0	3	26	13	67.2	±2.1

[a] The composite has not reached the required deformation of 0.25 mm up to 195 °C, which was the upper temperature limit of HDT test (explanation see in text)

Table 6 Glass-transition temperature of the composites determined by DSC-analysis (2nd heating)

Matrix	VIAPAL VUP4627 BEMT/56			AROPOL M105 TA		
Glass-mat	Glass-fibre content/vol%	Half c_p extrapolated/°C	Inflexion point/°C	Glass-fibre content/vol%	Half c_p extrapolated/°C	Inflexion point/°C
Ahlstrom	5	93	93	3	71	68
M 601	8	92	91	7	80	81
	11	94	93	13	78	82
Vetrotex	5	81	82	4	85	84
M134	7	81	80	6	79	80
	12	78	77	13	79	79

Fig. 6 The change of storage modulus of the composites with temperature
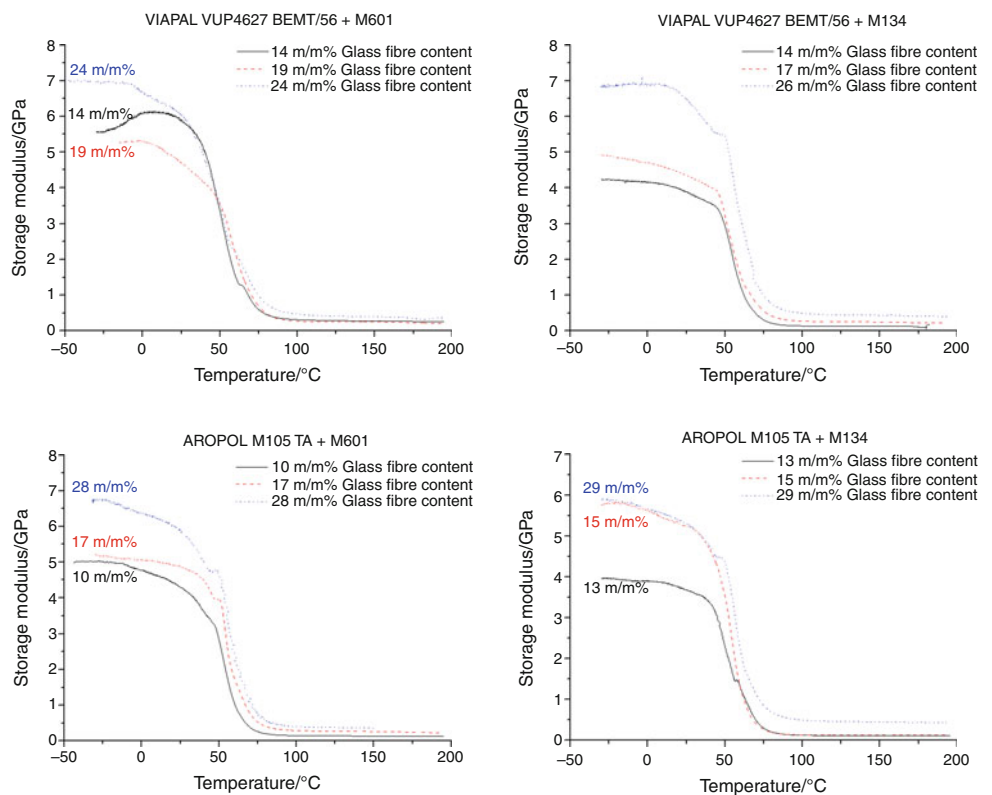
Table 7 Comparison of the HDT-values of the composites with the Takemori-temperatures (at which the storage moduli attain the value of 750 MPa)

Matrix	VIAPAL VUP4627 BEMT/56			AROPOL M105 TA		
Glass-mat	Glass-fibre content/ vol%	HDT/ °C	Temperature at 750 MPa/ °C	Glass-fibre content/ vol%	HDT/ °C	Temperature at 750 MPa/ °C
Ahlstrom	5	61	71	3	61	63
M 601	8	72	73	7	66	70
	11	>95	79	13	68	75
Vetrotex	5	62	65	4	61	66
M 134	7	68	70	6	62	64
	12	79	79	13	67	77

Fig. 7 The change of loss modulus of the composites with temperature
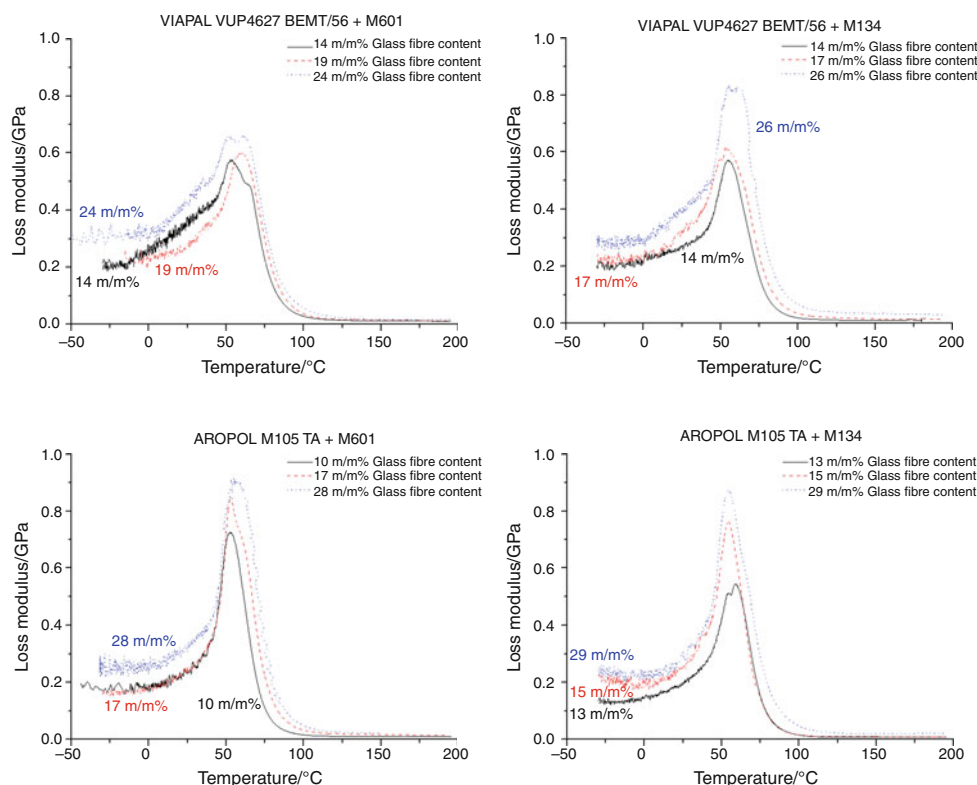
bending, the frequency 1 Hz. Dynamic force control was set by amplitude which was 20 μm, reached by 400 mN dynamic force. Static control force was set in tension which was 120%, therefore the static force was 500 mN. The test specimen have been cut to the size of 20 × 9 × 2 mm from those milled for HDT measurements in the way that the glass mat layers were parallel to the side of 127 mm of the HDT specimen.

Results

Thermogravimetric analysis

Both the cross-linked composites and the pure glass mats have been analysed by thermogravimetry. The TG thermograms of the two glass mats in purging nitrogen and oxygen are represented by Fig. 2 and the results are summarized in Table 1.

Both glass mats show a considerable decrease of mass at 334 °C in nitrogen and at 300 °C in oxygen, which detect the decomposition of the organic surface-treating agent. Since the temperature range of decomposition is the same for both glass mats, and the difference in residue after decomposition is within 1%, it may be concluded that the two glass mats have been surface-treated similarly. The slight decrease in mass (0.05–0.1 mass%) in the vicinity of 100 °C may be due to the moisture adsorbed on the surface of the glass mats. Since this adsorbed water is of small extent, it would not cause difficulties for the preparation of the composites.

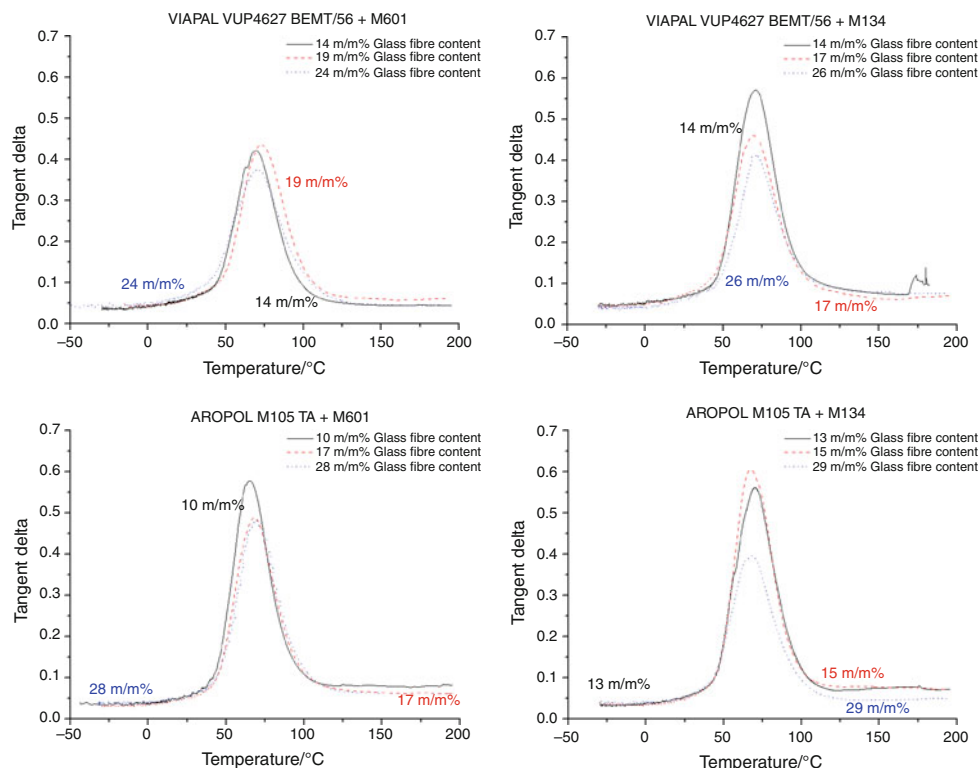**Fig. 8** The change of tanδ of the composites with temperature

Table 8 Peak temperatures of the tanδ—temperature diagrams of the composites

Matrix	VIAPAL VUP4627 BEMT/56		AROPOL M105 TA	
Glass-mat	Glass-fibre content /vol%	T_{peak}/ °C	Glass-fibre content/vol%	T_{peak}/ °C
Ahlstrom M 601	5	70.6	3	66.5
	8	74.3	7	69.3
	11	72.5	13	70.5
Vetrotex M 134	5	72.5	4	71.7
	7	71.0	6	69.2
	12	72.5	13	69.8

The main goal of thermogravimetric analysis of the composites was the exact determination of their glass-fibre content. Further on, the analysis enabled the comparison of their thermal and thermo-oxidative decomposition. Budrugeac and Segal investigated the thermo-oxidative degradation of an unsaturated polyester resin. They studied the effect of oxygen pressure on the kinetics of thermo-oxidative decomposition [28].

The curves in purging nitrogen and oxygen are represented by Figs. 3 and 4, the results are summarized in Tables 2 and 3, respectively.

The manual switching of the purging nitrogen to oxygen in the vicinity of 650 °C resulted in an instant loss of mass. The slight loss of mass around 100 °C may be due to the evaporation of the adsorbed water. Another decrease of mass could be detected in the vicinity of 210 °C, which may be attributed to the evaporation of volatile components such as the peroxide indicator. The overall decrease of mass until the onset of thermal decomposition is below 10 mass%, the onset of thermal decomposition is characteristic to the matrix and it is in the vicinity of 280–290 °C for both matrix polymers (Table 2).

The onset of thermo-oxidative decomposition is in the vicinity of 280–290 °C for both matrix polymers, similarly to thermal decomposition. There is a stepwise loss of mass of about 10% in the temperature range of 450–500 °C for each composite. With increasing glass-fibre content the peaks of the derivative curves shift towards higher temperatures, showing a delayed decomposition. The glass-fibre content of the composites has been determined from the residual mass after thermo-oxidative decomposition after correction with the quantity of the surface-treating agent detected from the curves of the pure glass mats. The results are summarized in Table 4.

Heat distortion temperature

The results of HDT measurements of the composites with different glass-fibre content are represented in Fig. 5 and summarized in Table 5.

At low glass-fibre concentrations, i.e. below 6 vol% (12 mass%), the glass-fibre content does not affect the

HDT of the composites, and it is in the vicinity of 60 °C. Above 6 vol% the HDT increases with increasing glass-fibre content for each composite system, but not at the same extent for the different systems. For the composites made with the matrix resin VIAPAL VUP4627 BEMT/56 the increase of HDT is much steeper than that of the composites containing the matrix AROPOL M105 TA. It can be assumed that the monomer composition of the two resins is different thus they have different interaction with the surface of the glass-fibre. It may also be concluded that HDT is determined by the simultaneous effect of the matrix and the fibre/matrix interphase. At low glass-fibre concentrations the effect of fibre/matrix interphase is of minor importance, the determining factor is the matrix. At higher glass-fibre concentrations the HDT-increasing effect of the interphase is more dominant. The latter, however, depends basically on the interaction between matrix and fibre, which is again in close relation with matrix properties.

It could also be observed that the behaviour of the composite made of VIAPAL VUP4627 BEMT/56 significantly depended on the type of glass-mat. Formulated with Ahlstrom M601 at glass-fibre content of 22 mass% (11 vol%) the composite has not even reached the required deformation of 0.25 mm up to 195 °C, which was the upper temperature limit of HDT test. In Table 5, the HDT of this system has been assigned to HDT > 95 °C, although real HDT value could not be measured. According to thermogravimetric analysis the glass-mat Ahlstrom 601 contained a bit higher quantity of surface treating agent, which might have enabled better interaction with the polymer matrix. During more repeated HDT measurements of this system, gradual deformation between 60 and 90 °C has been observed up to 0.2 mm. This has not changed on further heating up to 120 °C, then the specimen has straightened and on further heating its deformation has reversed in the opposite direction. At 195 °C the final deformation was 0.1 mm. The reason might have been the thermal relaxation of stresses during heating.

DSC-analysis

During the first DSC heating scans thermal events have been superimposed corresponding to the evaporation of adsorbed moisture and of other volatile components, as revealed by thermogravimetry, thus overlapping the relaxation transitions. Therefore, the glass-transition temperatures of the composites have been determined from the second DSC heating runs. The results are summarized in Table 6.

As detected by DSC the glass-transition temperature of the composites is in the temperature range of 68–94 °C. In accordance with the theoretical expectations they are characteristic to the cross-linked matrix polymer, the

glass-fibre content of the composites had no effect on T_g. It should be noted, however, that due to the small heat effect during glass-transition the T_g values are scattering.

Dynamic mechanical analysis

The temperature dependence of the storage modulus of the composites is represented in Fig. 6.

The steep decrease in the storage modulus is characteristic to the glass-transition range. Below the glass-transition all the composites have high modulus, in the range of 4–7 GPa, and they are significantly higher at higher glass-fibre content. The only exception is VIAPAL VUP4627 BEMT/56 with 8 vol% Ahlstrom M 601. The reason may be some fault in the test specimen. The glass-transition temperature range corresponding to the steep decrease of storage moduli is between 30 and 80 °C for all composites, and does not depend on the glass-fibre content. Above the glass-transition temperature range the value of storage moduli is between 0.1 and 1 GPa, and higher at higher glass-fibre content. The temperatures at storage modulus of 750 MPa (calculated by Takemori [26, 27]) increase with increasing glass-fibre content. This is in accordance with the HDT measurements (Table 7).

The loss modulus—temperature relations of the composites with different glass-fibre content are represented by Fig. 7.

The peak temperatures of the loss modulus of the composites are close to each other and do not depend on the glass-fibre content, as expected. The values of the loss modulus, however, increase with increasing glass-fibre content due to the higher inner friction of the reinforcing material. Some of the composites show twin peaks.

The temperature ranges of the tangent δ peaks are between 50 and 100 °C for each composite (Fig. 8).

The peak temperature of the tangent δ—temperature diagrams corresponds to the glass-transition temperature, and it is in the vicinity of 70 °C for all the composites. The exact values of the glass-transition temperatures determined by dynamic mechanical analysis are given in Table 8. These values are lower than those detected by DSC, although more accurate.

Summary

Thermogravimetric analysis enabled the determination of the glass-fibre content of the composites. The onset temperature of thermal and thermo-oxidative decomposition was similar, namely around 290 °C for each composite. Thermo-oxidative decomposition was delayed with increasing glass-fibre content. Thermogravimetric measurements served the determination of the glass-fibre

content and of the upper temperature limit for DSC, HDT and DMA measurements.

At low glass-fibre content (below 6 vol%, 12 mass%) the HDT is not effected by the glass-fibre concentration. Above 6 vol% glass-fibre content the HDT increased with the increase of glass-fibre concentration. The extent of increase depended on the selected glass-fibre/matrix components.

The enthalpy changes of the glass-transition of the composites were very small, therefore accurate detection by DSC analysis was not possible. Dynamic mechanical thermal analysis served more accurate determination of the glass-transition temperatures, which were lower, than those determined by DSC, namely in the vicinity of 70 °C for each composite. The glass-transition temperatures proved to be characteristic to the cross-linked matrix polymer, as expected, and are not affected by the type and content of the glass-fibre. The storage modulus increased with the glass-fibre content in the whole temperature range of DMA measurement, although the effect of glass-fibre content on the storage modulus was more significant below glass-transition, and around ambient temperature. The temperatures detected by dynamic mechanical thermal analysis corresponding to the storage modulus of 750 MPa are above the glass-transition and also increased with higher glass-fibre content in accordance with the real HDT measurements. It may be concluded, however, that the effect of reinforcement on the performance of the composite could be detected more reliably by HDT measurements, since it gives information on the deformation of the composites. Matrix-fibre interaction has an essential role on the performance and on the HDT of the composite materials.

References

1. Bruins PF, editor. Unsaturated polyester technology. London: Gordon and Breach; 1976.
2. Benjamin B. Structural design with plastics. New York: Van Nostrand Reinhold; 1982.
3. Scheirs J, Long TE, editors. Modern polyesters: chemistry and technology of polyesters and copolyesters. Chichester: John Wiley and Sons Ltd; 2003.
4. Solomon DH. Polyesterification. In: Solomon DH, editor. Step-growth polymerizations. New York: Marcel Dekker Inc.; 1972. p. 1–38.
5. Ham G, editor. Kinetics and mechanisms of polymerization. New York: Marcel Dekker Inc., Edward Arnold Ltd.; 1967.
6. Rudd CD, Long AC, Kendall KN, Mangin CGE. Liquid moulding technologies. Cambridge: Woodhead Publishing Limited; 1997.
7. Meyer RW. Handbook of pultrusion technology. New York: Chapman and Hall; 1985.
8. Tollens FR, Lee LJ. Cure analysis of unsaturated polyester resins using electron spin resonance spectroscopy, differential scanning calorimetry and rheometry. Polymer. 1993;34(1):29–37.
9. Lee DS, Han CD. The effect of resin chemistry on the curing behavior and chemorheology of unsaturated polyester resins. J Appl Polym Sci. 1987;34(3):1235–58.
10. Ramis X, Salla JM. Time-temperature transformation (TTT) cure diagram of an unsaturated polyester resin. J Polym Sci Part B Polym Phys. 1997;35(2):371–88.
11. Chandrasekhar S. Liquid crystals. Cambridge: Cambridge University Press; 1980.
12. Ciferri A, editor. Liquid crystallinity in polymers: principles and fundamental properties. New York: VCH Publishers, Inc.; 1991.
13. Wagatsuma M, Okazaki H, Yamamoto F, Yamakawa S. Thermoplastic Rubber/Liquid Crystal Polyester Dual Coextrusion Coating System for Plastics in Telecommunications IV.; 17-19 Sept. 1986; London1986. p. 8.1-8.9.
14. Furuta M, Yamaguchi T. Laminate of liquid crystal polyester resin composition. Sumimoto Chemical Company Limited, Japan; 1998.
15. Postema AR, Schipper GP, Scott JANC. Process for the preparation of self-reinforcing composite systems. Shell Int Research, assignee, Netherlands;1995.
16. Kim JY, Kang SW, Kim SH. Thermotropic liquid crystal polymer reinforced poly(butylene terephthalate) composites to improve heat istortion temperature and mechanical properties. Fibers Polym. 2006;7(4):358–66.
17. Kim JY, Kim SH. Structure and property relationship of thermotropic liquid crystal polymer and polyester composite fibres. J Appl Polym Sci. 2006;99(5):2211–9.
18. Hasegawa M, Sakamoto Y, Tanaka Y, Kobayashi Y. Poly(ester imide)s possessing low coefficients of thermal expansion (CTE) and low water absorption (III). Use of bis(4-aminophenyl)terephthalate and effect of substituents. Eur Polym J. 2010;46(7):1510–24.
19. Hussain F, Hojjati M, Okamoto M, Gorga RE. Polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater. 2006;47(17):1511–75.
20. Sepe MP. The usefulness of hdt and a better alternative to describe the temperature dependence of modulus in limitations of test methods for plastics, ASTM STP 1369. In: Peraro JS, editor. American Society for Testing and Materials. West Conshohocken;2000. p. 44–53.
21. Nielsen LE. Cross-linking—effect on physical properties of polymers. J Macromol Sci Part C Polym Rev. 1969;3(1):69–103.
22. Aklonis JJ, Knight WJM. Introduction to polymer viscoelasticity. New York: John Wiley and Sons; 1983.
23. Osswald TA, Hernández-Ortiz JP. Polymer processing. Munich: Carl Hanser Verlag; 2006.
24. Marossy K, Toth J. Anomalous behaviour of PVC–CPVC–CPE blends. Plast Rubber Compos. 2005;34(10):438–42.
25. Marossy K, Tarjanyi LE. Compatibility study of PVC and HT additives by the thermally stimulated discharge (TSD) method, vol. 4. London: Institute of Materials; 1994.
26. Takemori MT. Towards an understanding of the heat distortion temperature of thermoplastics. Polym Eng Sci. 1979;19(15):1104–9.
27. Takemori MT. Towards an understanding of the heat distortion temperature of thermoplastics. Technical Papers of the Annual Technical Conference–Society of Plastics Engineers; 1978.
28. Budrugeac P, Segal E. Thermooxidative degradation of an unsaturated polyester resin. The effect of oxygen pressure on the kinetics. J Therm Anal Calorim. 1997;49(1):183–91.