



Poly(trimethylolpropane trimethacrylate) modified with esters derivatives of 3-phenylprop-2-en-1-ol

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Abstract

The main objective of this paper was to study the influence of the diesters derivatives of naturally occurring alcohol: 3-phenylprop-2-en-1-ol, on the thermal, viscoelastic and mechanical properties of bulk poly(trimethylolpropane trimethacrylate) [poly(TRIM)]. The bulk poly(TRIM) networks were obtained by mixing trimethylolpropane trimethacrylate with 0.5, 1, 2, 3, 5, 10 and 20 mass% of diesters and polymerized in the presence of 1.5 mass% of benzoyl peroxide in the temperature range from 50 to 80 °C. Generally, bulk poly(TRIM) modified with esters derivatives of 3-phenylprop-2-en-1-ol was characterized by lower stiffness, lower glass transition temperature, lower thermal stability, lower hardness and heat deflection temperature values, and higher tensile strength and percentage elongation, especially for compositions containing higher diester content as compared to pure, bulk poly(TRIM).

Keywords Material testing · Mechanical properties · Thermal properties · Trimethylolpropane trimethacrylate (TRIM) · Esters of 3-phenylprop-2-en-1-ol

Introduction

Trimethylolpropane trimethacrylate (TRIM) is a water-insoluble, low-viscosity methacrylate monomer with a wide range of industrial applications. It has a high degree of functionality and low volatility, and thus, it is commonly applied as a reactive diluent in order to improve the strength, chemical resistance, heat resistance, hardness and weather resistance of many manufactured products. It forms both homopolymers and copolymers with various compounds, e.g. acrylic acid and its salts, amides, esters, methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters or drying oils [1–4]. The formed homopolymer: poly(trimethylolpropane trimethacrylate) [poly(TRIM)], is commonly used in the production of ultraviolet-curable inks, electron beam

irradiation-curable coatings, polymers and resins as a component of photopolymer and flexographic printing plates and photoresists and as an ingredient in acrylic glues, adhesives and anaerobic sealants. Additionally, it is used in the paper and wood impregnates, wire and cable extrusion, polymer-impregnated concrete, and polymer concrete structural composites [5–8]. Also, this multi-functional monomer with various monomers is generally applied in the production of porous microspheres suitable for chromatographic applications [9–11].

To improve the processing, performance and elasticity of polymer materials, the additives which make the material softer and more flexible are added [12–14]. The most generally applied plasticizers are phthalates and adipate esters, e.g. bis(2-ethylhexyl) phthalate, di-octylphthalate, diizodecyl phthalate, di-*n*-butylphthalate, butylbenzylphthalate, dioctyl adipate, bis(2-ethylhexyl) adipate. Also, stearates as plasticizers for lacquers and rubbers and esters of rosin are used [15–18]. Most of them have toxic properties for human, and recently, the studies on the new, non-toxic and biodegradable materials which could replace harmful plasticizers are developed [19]. In recent years, the intensive studies on the utilization of the epoxidized vegetable oils and biodiesel oils as plasticizers are conducted

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[20, 21]. Also, eco-friendly plasticizers such as triacetin, tripropionin, triethyl citrate, tributyl citrate, tributyl 2-acetyl citrate and poly(ethylene glycol) of low molecular mass are known [22]. Recently, the studies on the utilization of diesters derivatives of 3-phenylprop-2-en-1-ol as suitable plasticizers for linear polymers such as polystyrene were performed [23].

The main objective of this paper is to study the possibility of using diesters derivatives of 3-phenylprop-2-en-1-ol obtained in one-step polycondensation process of a stoichiometric ratio of 3-phenylprop-2-en-1-ol and chosen acidic reagent: succinic anhydride or sebacic acid as new plasticizers for cross-linked polymeric materials. The influence of the diesters concentration on the thermal, viscoelastic and mechanical properties of bulk poly(TRIM) networks has been studied and discussed.

Experimental

Materials

Diesters derivatives of 3-phenylprop-2-en-1-ol were obtained during catalysed esterification process of 2 mol of 3-phenylprop-2-en-1-ol (98%, Fluka) with 1 mol of acidic reagent. As acidic reagents, succinic anhydride (99%, Merck) and sebacic acid (98%, Merck) were used. The reaction was carried out at 130 °C, under reduced pressure. Butylstannic acid (Arkema Inc., the USA) was used as a catalyst in the amount of 0.05 mass% [24]. Trimethylolpropane trimethacrylate (TRIM) was from Aldrich. The vinyl monomer was washed with 10% solution of NaOH in order to remove an inhibitor, and then it was dried over anhydrous magnesium sulphate and drained off. Benzoyl peroxide was from POCh, Gliwice, Poland. Figure 1 presents the structure of the obtained diesters.

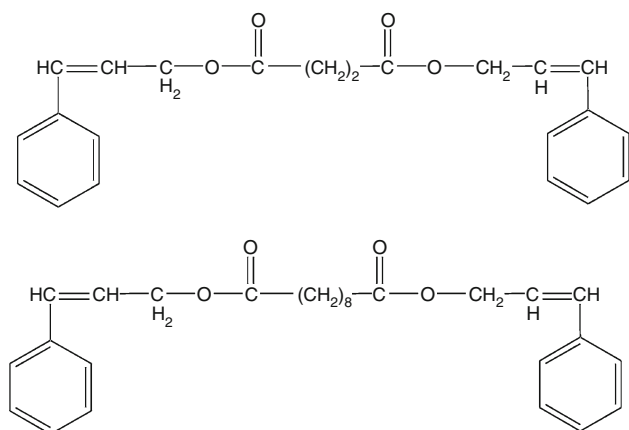


Fig. 1 Structure of diesters

Polymerization procedure

The polymerization process of components mixture containing from 0.5 to 20.0 mass% of diesters derivatives of 3-phenylprop-2-en-1-ol was carried out in the presence of benzoyl peroxide (used in the amount of 1.5 mass%). Initially, the bulk polymerization process was performed at 50 °C and then the polymerization temperature was gradually increased to 80 °C. The materials were kept at 80 °C until no additional post-curing signal was observed from DSC curves.

Methods

Differential scanning calorimetry analysis was performed with the use of a DSC 204 calorimeter, Netzsch, Germany, operating in a dynamic mode. DSC measurements were taken in Al pans with the pierced lid. Two dynamic scans of the samples (10 mg) were performed at a heating rate of 10 °C min⁻¹ under argon atmosphere (25 mL min⁻¹). The first was from -20 to 200 °C, and the second one from -20 to 550 °C.

Dynamic mechanical analysis (DMA) was performed with the use of a Dynamic Mechanical Analyzer Q 800 TA Instruments, the USA, equipped with a double-cantilever device (support span of 35 mm). The temperature scanning from -60 to 200–250 °C with a constant heating rate of 6 °C min⁻¹ at an oscillation frequency of 10 Hz was conducted. The storage modulus ($E'_{20\text{ °C}}$), $\tan\delta_{\text{max}}$ and $\tan\delta_{\text{max}}$ height were determined.

Heat deflection temperature (HDT) was evaluated using an HDT 3 VICAT apparatus, Ceast SpA, Italy. The rectangular profile of the samples 10 mm wide, 4 mm thick and 70 mm length was submerged in an oil bath and heated (heating rate 2 °C min⁻¹) from 20 °C until the 2% deflection of the sample under a load of 1.8 MPa occurred.

Hardness according to Brinell was determined by means of a hardness tester HPK, Germany. In this procedure, a steel ball of 5 mm diameter was hydraulically loaded on the material test surface with a load (F) of 36.5 kgf (0, 357, 942, 725 kN). The load was applied for 60 s. Then, the resulting depression in cm was read. The hardness (HK) was calculated using the equation: $\text{HK} [\text{MPa}] = F/1.57 * h * 0.098066 = F_1 * 0.098066$, where F is load in kgf, h —depression in cm, and $F_1 = F/1.57 * h$.

Mechanical properties were examined using a strength machine, Zwick Roell Z010, Germany, for the following samples: 10 mm wide and 4 mm thick. Measurements were taken at room temperature. The cross-head speed was 2 mm min⁻¹. The initial grip separation was 50 mm. The ultimate tensile strength (δ) and percentage elongation at break (ϵ) were determined.

Table 1 DSC data for cured materials containing dicinnamyl succinate

Diester/wt%	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max1}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	$\Delta H_1/\text{Jg}^{-1}$
0	305	457	493	463.8
0.5	302	451	495	446.6
1	290	458	494	454.2
3	270	454	495	486.8
5	275	451	492	516.0
10	270	445	490	532.5
20	264	437	485	513.3

Table 2 DSC data for cured materials containing dicinnamyl sebacate

Diester/wt%	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max1}}/^{\circ}\text{C}$	$T_{\text{end}}/^{\circ}\text{C}$	$\Delta H_1/\text{Jg}^{-1}$
0	305	457	493	463.8
0.5	300	454	493	451.2
1	295	451	495	475.1
3	295	450	495	497.7
5	278	449	490	532.9
10	270	445	496	544.7
20	265	443	490	554.1

Thermal analysis was performed on a STA 449 Jupiter F1, Netzsch, Germany, using Al_2O_3 crucibles and the sample mass ca. 10 mg. The analyses were performed under helium atmosphere (25 mL min^{-1}) in the temperature range of 40–800 $^{\circ}\text{C}$ and with a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

Table 3 Viscoelastic and mechanical properties, hardness and heat deflection temperatures for cured materials containing dicinnamyl succinate

Diester/mass%	$E'_{20 \text{ } ^{\circ}\text{C}}/\text{MPa}$	$\tan\delta_{\text{max}}/^{\circ}\text{C}$	$\tan\delta_{\text{max}}$ height	δ/MPa	$\varepsilon/\%$	HK/MPa	HDT/ $^{\circ}\text{C}$
0	3200	143	0.038	60	5	177	110
0.5	3150	140	0.065	62	5	176	110
1	3100	135	0.073	65	6	176	105
3	2860	130	0.076	70	8	175	103
5	2750	128	0.078	78	11	175	100
10	2500	125	0.085	82	15	175	100
20	2080	120	0.098	94	23	153	90

Table 4 Viscoelastic and mechanical properties, hardness and heat deflection temperatures for cured materials containing dicinnamyl sebacate

Diester/mass%	$E'_{20 \text{ } ^{\circ}\text{C}}/\text{MPa}$	$\tan\delta_{\text{max}}/^{\circ}\text{C}$	$\tan\delta_{\text{max}}$ height	δ/MPa	$\varepsilon/\%$	HK/MPa	HDT/ $^{\circ}\text{C}$
0	3200	143	0.038	60	5	177	110
0.5	3120	138	0.068	63	6	177	110
1	2950	135	0.079	65	6	174	105
3	2730	128	0.083	74	9	172	100
5	2620	125	0.096	78	12	170	95
10	2190	123	0.112	84	17	166	90
20	2010	115	0.125	96	25	121	82

Results and discussion

Below the temperature of 200 $^{\circ}\text{C}$, no exo- or endothermic signals from the DSC results gathered for bulk poly(TRIM), and poly(TRIM) containing diesters derivatives of 3-phenylprop-2-en-1-ol were observed (Tables 1 and 2). It confirmed that the samples are highly cured and testified to the absence of free monomer. No evaporation of components of the compositions was observed. In addition, due to high conversion of double bonds in the prepared networks, there was a lack of the glass transition region in DSC curves. In DSC curves above temperatures of 300 $^{\circ}\text{C}$, one endothermic signal was indicated. It was directly connected with the decomposition process of the studied materials [25–27].

The characteristic values of DSC signal such as onset decomposition temperature (T_{onset}), maximum peak temperature (T_{max}), end decomposition temperature (T_{end}) and the enthalpy of decomposition (ΔH) are given in Tables 1 and 2. The presented data suggested that higher content of diesters had higher influence on the characteristic temperatures. The T_{onset} and T_{max} were shifted to lower temperatures as the diester content increased, which might be due to the lower thermal stability of diesters than that of pure poly(-TRIM). However, more differences were observed when compared to the values of the decomposition enthalpy. As the diester content increased, the enthalpy of the decomposition process of the materials gradually increased. It confirmed higher stability of the bonds existing in poly(TRIM)

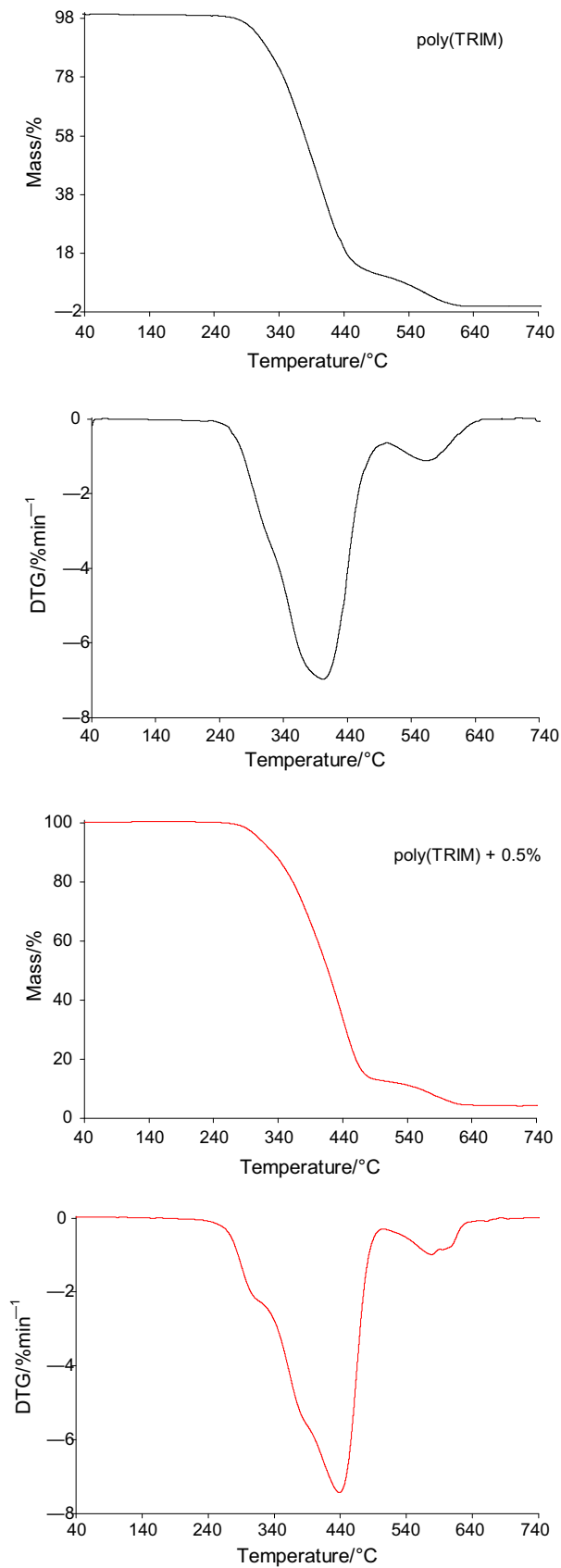


Fig. 2 TG and DTG curves of the prepared materials

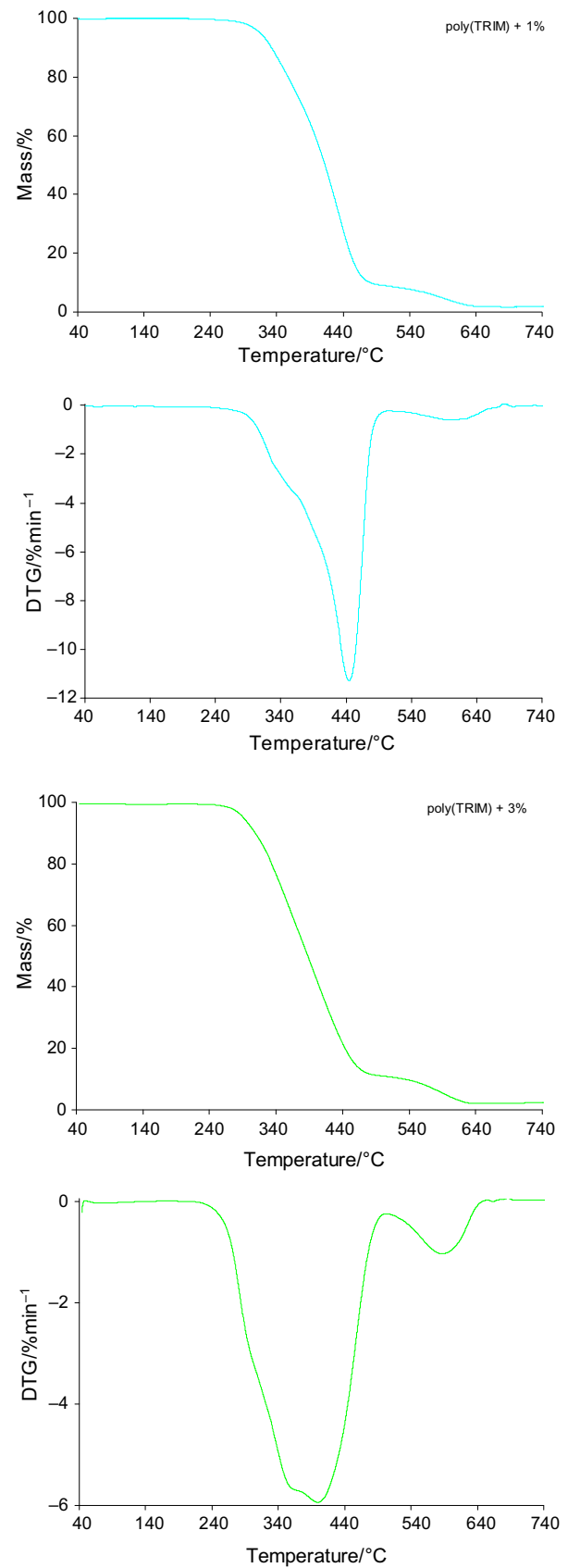


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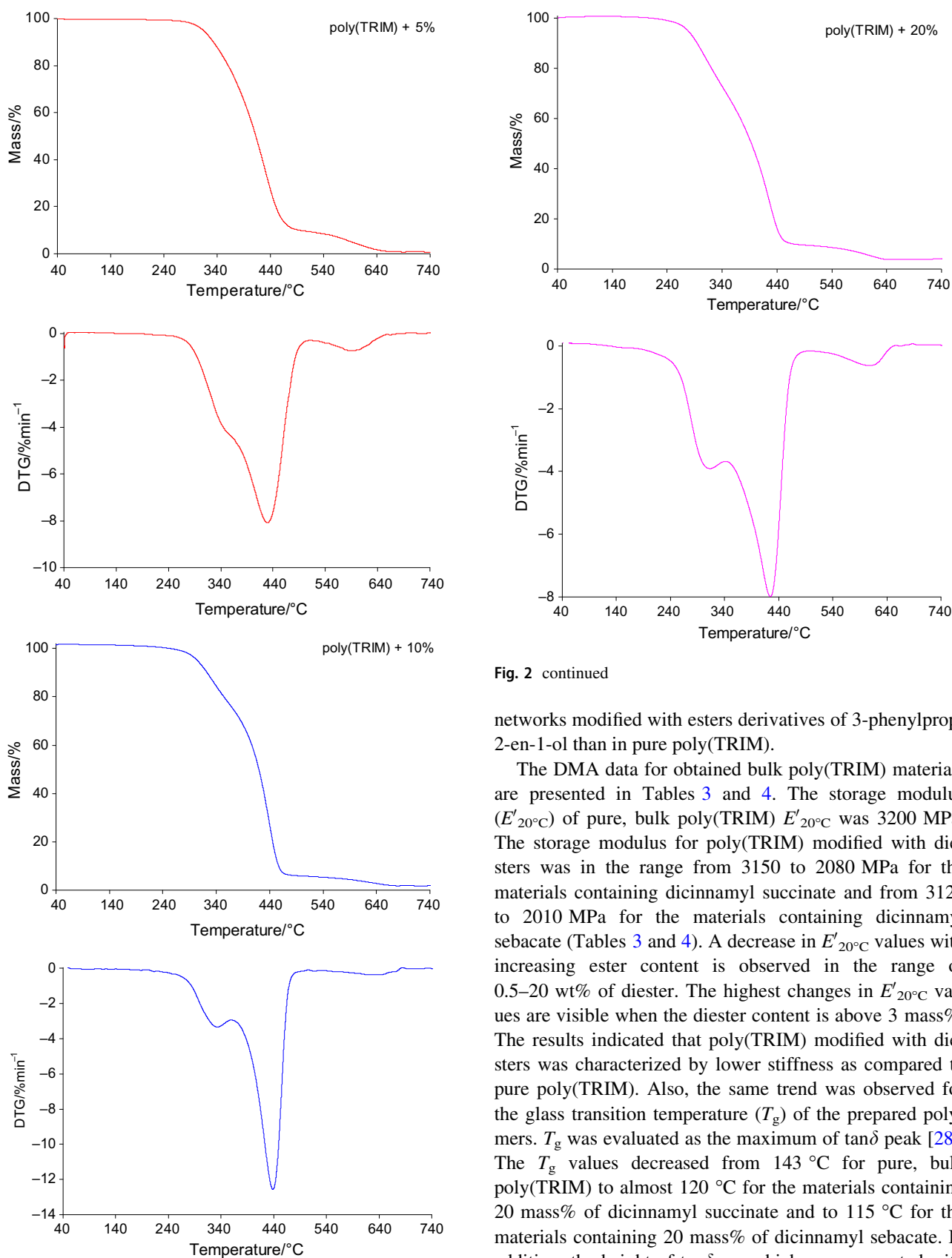


Fig. 2 continued

Fig. 2 continued

networks modified with esters derivatives of 3-phenylprop-2-en-1-ol than in pure poly(TRIM).

The DMA data for obtained bulk poly(TRIM) materials are presented in Tables 3 and 4. The storage modulus ($E'_{20^{\circ}\text{C}}$) of pure, bulk poly(TRIM) $E'_{20^{\circ}\text{C}}$ was 3200 MPa. The storage modulus for poly(TRIM) modified with diesters was in the range from 3150 to 2080 MPa for the materials containing dicinnamyl succinate and from 3120 to 2010 MPa for the materials containing dicinnamyl sebacate (Tables 3 and 4). A decrease in $E'_{20^{\circ}\text{C}}$ values with increasing ester content is observed in the range of 0.5–20 wt% of diester. The highest changes in $E'_{20^{\circ}\text{C}}$ values are visible when the diester content is above 3 mass%. The results indicated that poly(TRIM) modified with diesters was characterized by lower stiffness as compared to pure poly(TRIM). Also, the same trend was observed for the glass transition temperature (T_g) of the prepared polymers. T_g was evaluated as the maximum of $\tan\delta$ peak [28]. The T_g values decreased from 143 °C for pure, bulk poly(TRIM) to almost 120 °C for the materials containing 20 mass% of dicinnamyl succinate and to 115 °C for the materials containing 20 mass% of dicinnamyl sebacate. In addition, the height of $\tan\delta_{\text{max}}$, which was connected with the mobility of the resin molecules [29–32], increased as

Table 5 TG and DTG data for cured materials containing dicinnamyl succinate

Diester/mass%	First weight loss/%	IDT ₁ /°C	T _{max1} /°C	FDT ₁ /°C	Second weight loss/%	T _{max2} /°C	FDT ₂ /°C
0	89.7	296	402	486	10.3	563	630
0.5	87.4	310	308/438	495	8.3	577	670
1	91.0	320	350/432	500	7.3	600	640
3	89.4	291	362/400	497	8.5	589	630
5	93.2	313	348/443	490	6.0	596	682
10	94.2	305	331/439	481	4.0	643	685
20	90.5	280	308/426	476	5.7	612	634

IDT initial decomposition temperature (expressed as the temperature where 5% of mass loss is observed), T_{max} temperature at the maximum degradation rate, FDT final decomposition temperature

Table 6 TG and DTG data for cured materials containing dicinnamyl sebacate

Diester/mass%	First mass loss/%	IDT ₁ /°C	T _{max1} /°C	FDT ₁ /°C	Second mass loss/%	T _{max2} /°C	FDT ₂ /°C
0	89.7	296	402	486	10.3	563	630
0.5	95.0	344	366/452	494	2.9	590	776
1	90.6	314	342/427	499	8.7	598	645
3	92.0	315	340/425	495	8.0	602	640
5	91.0	315	345/430	492	7.0	592	627
10	92.8	305	332/436	485	5.3	645	695
20	93.8	279	308/425	480	5.8	628	660

IDT initial decomposition temperature (expressed as the temperature where 5% of mass loss is observed), T_{max} temperature at the maximum degradation rate, FDT final decomposition temperature

diester content increased. Also, compositions containing diester with higher chain lengths exhibit lower values of storage modulus and glass transition temperature, and higher values of $\tan\delta_{\max}$ height comparing to pure, bulk poly(TRIM) and poly(TRIM)-based materials containing ester with lower chain length.

The values of the heat deflection temperature under load (HDT) and hardness values (HK) are presented in Tables 3 and 4. The small changes in HDT and HK values for the materials containing diesters in the range from 0.5 to 10 mass% were indicated. The significant drop of HDT values from 110 °C for bulk, pure poly(TRIM) to 90 and 82 °C for poly(TRIM) containing 20 mass% of suitable diester was observed. The drop of HDT values of compositions containing poly(TRIM) and diesters indicated that the materials were more vulnerable to deformation under the specific load at lower temperatures. Also, the same trend was visible for HK values. The reduction in HDT and HK values for higher diester content confirmed obtaining less brittle and more soft materials, which was the result of the disruption and/or weakness of the

secondary bonds between poly(TRIM) chains by plasticizer and thus the creation of more space for polymer chain motions.

In addition, the tensile strength (δ) and percentage elongation (ϵ) appeared to be increasing from 60 MPa and 5% to almost 94–96 MPa and 23–25% as diesters concentration increased (Tables 3 and 4).

The pure poly(TRIM) decomposed at least in two main stages during pyrolysis (Fig. 2, Tables 5 and 6). However, the asymmetrical shape of DTG curves of pure poly(TRIM) may also suggest that their decomposition runs as multi-step processes with two or three steps in the temperature range from c.a. 240 °C to c.a. 500 °C. The addition of diesters derivatives of 3-phenylprop-2-en-1-ol to poly(TRIM) generally leads to an insignificant increase in IDT temperatures for composition containing small amount of diesters. However, a displacement of the initial decomposition temperature (IDT) of the obtained materials towards lower temperatures as the diester content increased was indicated. As shown in Fig. 2, the materials containing esters decomposed in two main stages. The first stage

appeared from c.a. 230 °C to about 500 °C with $T_{\max 1}$ given in Tables 5 and 6. Between those temperatures, one non-well-separated DTG signal composed of at least two or three degradation steps was observed. The mass loss under this stage was significant. It ranged from 87.4 to 95.0%. The mass loss was almost independent on the type of diester added and their content. This stage was connected with the decomposition of the ester and carbon–carbon bonds existing in the polymer network. The second decomposition stage was observed at higher temperatures ($T_{\max 2}$) above 550 °C. The mass loss was from 2.9 to 8.7%. It was probably the result of the carbonization process of polymeric residue formed after the first decomposition stage [33].

Conclusions

The influence of diesters derivatives of 3-phenylprop-2-en-1-ol on the properties of bulk poly(TRIM) has been studied. The decrease in the storage modulus ($E'_{20^\circ\text{C}}$), glass transition temperature (T_g), heat deflection temperature under load (HDT), hardness (HK) and thermal stability, and the increase in the tensile strength (δ) and percentage elongation (ε) of the prepared materials, as diester content increases, suggest that diesters act as plasticizers. Based on the obtained results, one can conclude that the presence of diesters in compositions causes the occupation of intermolecular spaces between poly(TRIM) chains and thus the reduction and/or disruption of secondary forces among polymer chains. It leads to changes in the three-dimensional organization of poly(TRIM) and the reduction in the energy needed for molecular motions of polymer chains. As a consequence, the addition of diesters improves the flexibility and elongation and reduces the fragility of the prepared poly(TRIM) materials. In conclusion, due to its influence on the properties of poly(TRIM), diesters could find their place as more environmentally friendly plasticizers, as compared to commercially applied low molecular mass compounds, for other methacrylate cross-linked materials.

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