

Influence of TDI Concentration on the Properties of Unsaturated Polyester Resins

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ABSTRACT: Three different unsaturated polyester resins were modified by toluene diisocyanate (TDI). All the resins studied were commercially available. One, 2, and 3% additions of TDI caused important changes of the resins properties. With an increase of TDI concentration gelation times increased. Suppression of the exotherm peaks—desired effect from practical point of view—was observed. Unfortunately, increase of TDI concentration caused enormous increase of the resins viscosity. Additionally the resins with 3% of TDI exhibit thixotropic properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1201–1206, 2001

Key words: unsaturated polyester resin; modification with toluene diisocyanate; TDI; thermomechanical properties

INTRODUCTION

Unsaturated polyester resins are increasingly used as composite matrices in the building of large ships, pressurized water pipes, etc., as they are inexpensive and easy to process materials.¹

Unfortunately, these resins contain ester groups in their chains, especially maleate and phthalate groups, characterized by a relatively high sensitivity to hydrolysis compared, for instance, to vinyl esters containing methacrylic esters.^{2–5} Additionally, acidic and alcoholic chain ends of the resins are also chemically sensitive. Consequently, an embrittlement of the fiber-reinforced unsaturated polyester composites exposed to wet media occurs. To improve the mechanical properties of the resins and laminates derived from them, different modification methods are applied. Alcoholic end groups of the resin can be

blocked by isocyanates that form covalent urethane bonds.^{6–10} The reaction between the hydroxyl chain ends and the isocyanate groups of a di- or polyisocyanate will result in a molar mass increase and, consequently, in a viscosity increase. The alternative thickening process involves an interaction of carboxylic end groups of unsaturated polyester prepolymers with alkaline earth oxides or hydroxides to increase the viscosity of uncrosslinked reactive systems during maturation, just after mixing.¹¹ Similar to the alkaline earth oxide-thickening process, the control of compound viscosity by isocyanate thickening strongly depends on the following parameters: molar mass and molar mass dispersity of unsaturated polyester prepolymers, hydroxyl functionality of polyester prepolymers, type and amount of polyisocyanate, and amounts of fillers and fibers.^{11–15} The purpose of the chemical thickening is to provide a tack-free prepreg that is stiff enough to permit easy material handling and also to provide sufficient resin viscosity to carry the glass fibers to the extremities of the mould during the mold-filling stage in a curing process.

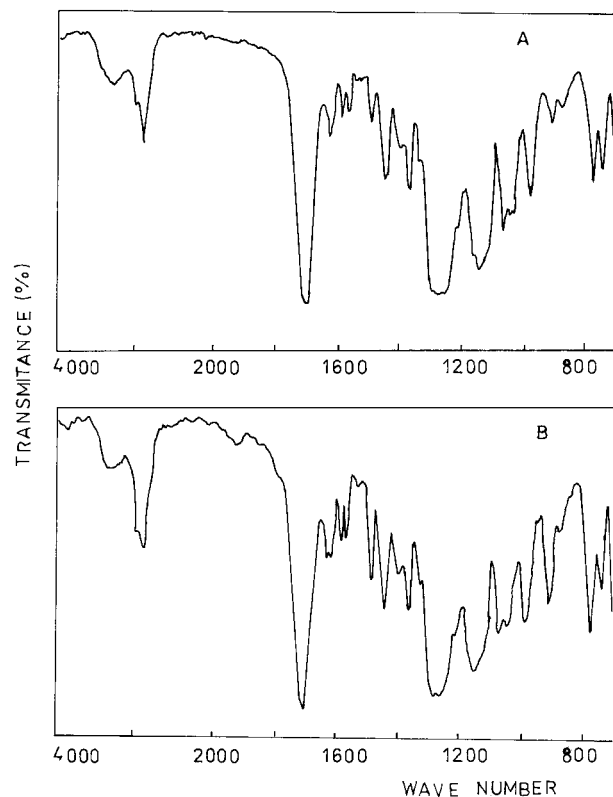
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Table I Properties of 55% Styrene Solution of the Parent Resins

Properties	Resin		
	D-1101	D-1103	D-1104NR
Density (g/cm ³)	1.2	1.1	1.1
Viscosity (mPas ⁻¹)	120	390	250
Acid value (mg KOH/g)	15	20	25
Hydroxyl value (mg KOH/g)	29	22	16
Gelation time (min)	27	18	10
Peak exotherm temperature (°C)	160	105	200

The aim of this article is to determine the influence of the amount of toluene isocyanate on the properties of different unsaturated polyester resins. The resins are commercially available. Two of them (D-1101 and D-1103) are based on phthalic and maleic anhydrides and ethylene and diethyl-

**Figure 1** FTIR spectra of the resin D-1101; without TDI (A), with 3% of TDI (B).**Table II** Gelation Times and Peak Exotherm Temperatures of the Resins Modified by Different Amounts of TDI

TDI (%)	Gelation Time (min)	Peak Exotherm Temperature (°C)
D-1101 (60%)		
1	23.2	92.8
2	20.0	89.0
3	—	—
(55%)		
1	24.3	83.9
2	17.5	62.1
3	—	—
(50%)		
1	16.7	49.3
2	9.5	48.0
3	—	—
D-1103 (60%)		
1	15.0	44.2
2	10.0	42.9
3	6.0	—
(55%)		
1	14.0	32.6
2	6.0	28.8
3	4.0	—
(50%)		
1	8.0	31.4
2	6.0	—
3	4.0	—
D-1104NR (55%)		
1	8.0	168.2
2	5.0	132.0
(50%)		
1	6	135.0
2	—	—

ene glycols, while D-1104NR is synthesized from the mixture of the mentioned glycols and the product of glycolysis of waste poly(ethylene terephthalate) (PET).

EXPERIMENTAL

Materials

Unsaturated polyester resins D-1101, D-1103 and D-1104NR came from Chemical Plant "Polifarb Becker Dębica S.A." (Dębica, Poland). Commercial grade toluene diisocyanate (TDI) containing 80% of 2,4- and 20% of 2,6-isomers was from Chemical Plant "Organika-Sarzyna" (Nowa Sarzyna, Poland). Luperox (50% solution of methyl ethyl ketone hydroperoxide in dimethyl phtha-

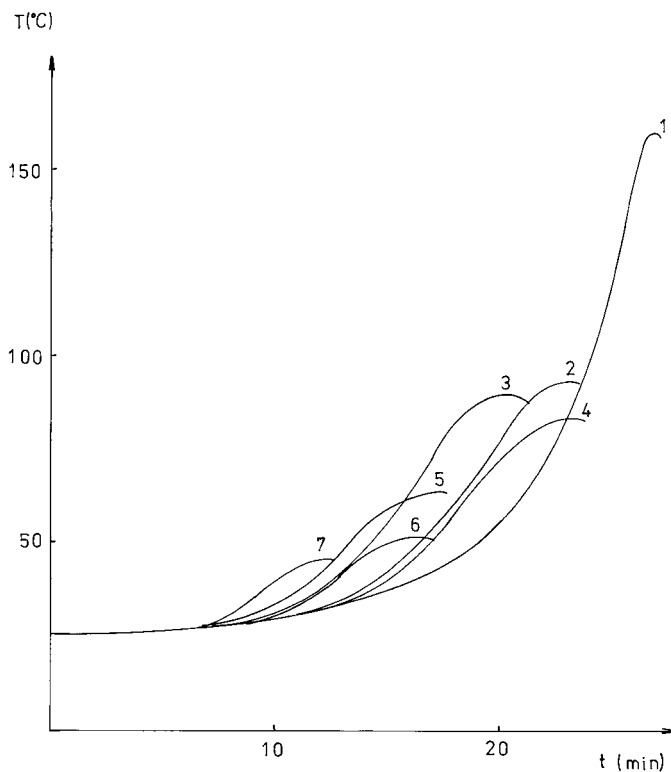


Figure 2 Dependence of the exotherm peak temperature ($^{\circ}\text{C}$) vs. time (min) and concentration of TDI for the resin D-1101. 1 = parent resin; 2 = 1%, 3 = 2% of TDI in 60% resin; 4 = 1%, 5 = 2% of TDI in 55% resin; 6 = 1%, 7 = 2% of TDI in 50% resin.

late) was bought from Luperox (Günzburg, Germany). Styrene and cobalt octanoate (1% Co in styrene) were from POCh (Gliwice, Poland).

Modification of Unsaturated Polyester Resins

Before modifications, the resins were dissolved in styrene. Three different styrene solutions of each resin were prepared. They contained 40, 45, and 50% of styrene. Then, each unsaturated polyester resin styrene solution was modified by the addition of 1, 2, and 3% of TDI.

The exemplary procedure is the following: 99 g of unsaturated polyester styrene solution was heated to the temperature of 60°C and then 1 g of TDI was added while stirring. The mixture was stirred at this temperature for ~ 2 h. The reaction was controlled by the change of the NCO groups content. The process was over when NCO value was equal to zero.

Curing Procedure

The resins were cured using 0.25% of cobalt octanoate and 1% of Luperox. The resins were pre-

liminarily cured at room temperature for 16 h and then postcured at 80°C for 4 h.

Characterization

The infrared (IR) spectra were recorded on a FTIR Perkin-Elmer 1700 spectrometer using KBr pellets. Mechanical and thermal properties were performed according to the Polish Standards: heat resistance by the Martens method (PN-90/C-89025), impact strength by the Charpy method (PN-81/C-89029), and ball indentation hardness (PN-84/C-89030).

Thermal stability of the resins was determined using a MOM derivatograph (Budapest, Hungary) at a heating rate of $5^{\circ}\text{C}/\text{min}$. in a range from 20 to 1000°C in the air.

The initial decomposition temperatures were determined from the course of the TG curves. The gelation times and peak exotherm temperatures of the investigated resins were determined in a temperature-controlled bath (25°) according to Polish Standard PN-75/C-89082. Changes of the resins viscosity were measured on a Brookfield DV-III programmable rheometer using one type

Table III Viscosities and Thixotropic Gelatinization Times of the Studied Resins

TDI (%)	Viscosity, η (mPs)	Gelatinization Time (min)
D-1101 (60%)		
	429	
1	[429]	n/o
	3280	
2	[3292]	25
3	—	—
(55%)		
	450	
1	[434]	n/o
	6335	
2	[2092]	32
3	—	—
(50%)		
	530	
1	[527]	n/o
	4002	
2	[1856]	50
3	—	—
D-1103 (60%)		
	850	
1	[850]	n/o
	2180	
2	[1184]	300
3	—	—
(55%)		
	822	
1	[822]	n/o
	2202	
2	[1125]	95
3	—	—
(50%)		
	1374	
1	[844]	n/o
	3517	
2	[1602]	45
	562720	
3	[8050]	27
D-1104NR (55%)		
	480	
1	[480]	n/o
	2680	
2	[913]	90
(50%)		
	350	
1	[350]	n/o
2	—	—

In brackets—viscosity of the resin sample after shaking.
n/o—not observed.

of spindle. These measurements were made at 25°C both for the static samples and shaken for 5 min. Thixotropic properties of the resins were

determined as follows:¹⁶ Test tubes with the resin samples were shaken in a shaker to break down the thixotropic structure. Then they were maintained in a water bath at 25°C to gelatinize. The times of gelatinization were measured. The experiment lasted 1 week.

RESULTS AND DISCUSSION

Properties of 55% styrene solutions of the resins used for modification with TDI are presented in Table I. These data indicate that their basic properties are quite different. Above all, they are characterized by different reactivities. Among them the unsaturated polyester resin D-1104NR has the greatest acid value, while D-1101 has the smallest one. Simultaneously, the latter has the greatest hydroxyl value. FTIR spectrum of this resin is presented in Figure 1. For comparison, in this figure, spectrum of the resin modified by 3% of TDI was added. On the spectrum of modified resin doublet absorption bands at 1655–1620 cm^{-1} typical for amide groups are visible. On both spectra the band of hydroxyl groups at 3560 cm^{-1} are present.

As expected, blocking of reactive hydroxyl groups in the studied resins significantly changed their properties. In Table II, gelation times and peak exotherm temperatures for the resins modified by different amount of TDI are presented. Generally gelation times decrease with an in-

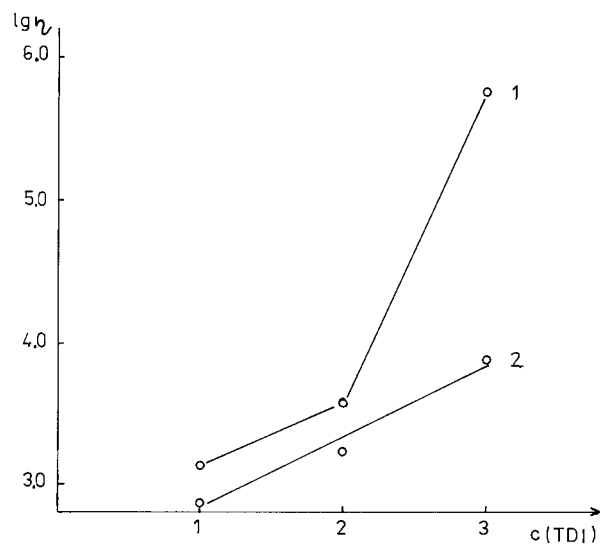


Figure 3 Changes of the resin D-1101 viscosity; curves: 1 = before shaking, 2 = after shaking.

Table IV Thermomechanical Properties of the Resins Studied

TDI (%)	Initial Decomposition Temperature (°C)	Thermal Resistance According to Martens (°C)	Impact Strength According to Charpy (kJ/m ²)	Ball Indentation Hardness (MPa)
D-1101 (60%)				
1	280	90	6.9	138.0
2	290	63	3.4	130.8
3	275	—	—	—
(55%)				
1	295	68	5.0	132.8
2	300	62	3.7	115.1
3	250	—	—	—
(50%)				
1	240	80	3.7	120.6
2	250	70	3.5	91.3
3	270	—	—	—
D-1103 (60%)				
1	230	65	4.3	146.7
2	250	66	5.7	95.9
3	280	68	6.2	—
(55%)				
1	250	67	3.6	140.9
2	270	70	7.1	82.5
3	280	—	—	—
(50%)				
1	280	70	—	—
2	260	70	—	—
3	250	79	3.8	88.0
D-1104NR (55%)				
1	300	72	20.1	133.5
2	300	75	14.3	132.0
(50%)				
1	300	67	9.0	130.3
2	—	—	—	—

crease of TDI concentration but exothermic effects of curing become smaller (Figure 2). Suppression of the exotherm peak is very important especially if thick-walled reinforced polyester articles are manufactured that can distort when the exotherm effects are so high.¹⁷ Unfortunately, with an increase of TDI concentration an extraordinary increase of the resin viscosity is observed (Table III). The addition of 1% TDI caused rather beneficial changes of the resin viscosity. Two percent of TDI caused enormous viscosity increase, while the resins with 3% of TDI formed a highly ordered structure that could be disturbed only by shaking. The only exception was 50% styrene solution of the resin D-1103 for which viscosity determination before shaking was possible. In Figure 3, relation $\lg \eta$ vs. concentration of TDI for this resin is presented. Nonlinear course of this rela-

tion suggests thixotropic character of this resin solutions. The observed thixotropy was also confirmed by determination of gelatinization times (Table III). From these data one can see that above 1% of TDI all the resins studied gelatinize. This phenomenon is independent of styrene concentration. When concentration of TDI reaches 3% thixotropic gelatinization times are very short (~ 30 min).

The observed thixotropy showed that determination of some properties of the resins in a cured state was impossible (Table IV). Comparing thermomechanical properties one can see that for the resin D-1101 the increase of TDI concentration caused a decrease of thermal resistance according to Martens, while for D-1103 this relationship is opposite. It seems that the resin D-1104 behaves similarly. This resin is also characterized by high

impact resistance. Values of impact strength according to Charpy are significantly greater than those for other resins. For all the resins studied, the increase of TDI concentration diminished their hardness.

CONCLUSIONS

The data presented here suggest that the addition of TDI to the studied resins cannot be greater than 1%. This amount is enough from a practical point of view. For higher concentrations of TDI undesirable changes in the resins properties are observed: enormous viscosity increase, and thixotropic properties for the resins containing 3% of TDI.

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