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Effect of melting point of the acid used for esterification of hyperbranched polyglycerol on homogeneity of polyester

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Abstract: *Effect of melting point of the acid used for esterification of hyperbranched polyglycerol on homogeneity of polyester.* A hyperbranched polyglycerol containing cyclic carbonates was esterified with three aliphatic and three aromatic dicarboxylic acids. It was shown that the melting point of an acid, determined homogeneity or inhomogeneity of the adhesive system. Analyses of microstructure of the respective polyesters were made.

Keywords: polyglycerol, cyclic carbonates, estrification

INTRODUCTION

In 1959 Tarbell and Longosz found that cyclic carbonates might undergo esterification reactions with dicarboxylic acids. Later, Parzuchowski et al. (2007) successfully synthesized hyperbranched polyglycerols containing cyclic carbonates and used them as curing agents for epoxies.

More recently, Mamiński et al. (2011a,b) reported on *in situ* esterification of hyperbranched polyglycerols with dicarboxylic acids. The approach was aimed at polyesterification performed within a bond line during wood bonding. Hyperbranched polyglycerol HBP-1W bearing the polyether backbone and cyclic carbonates on the shell of molecule (structure shown in Fig. 1) was a subject of polyesterification with aliphatic and aromatic dicarboxylic acids: adipic, sebacic, succinic, phthalic, isophthalic and terephthalic.

The results of bonding revealed an great effect of melting point of the acid used for esterification on bonding ability of the system. Thus, in this work microstructure of the cured polyester was analyzed.

MATERIALS AND METHODS

HBP-1W highly viscous (1300 Pa·s at 20ºC) dark yellow oil of theoretical molecular weight 953 g/mol and 3 cyclic carbonate groups was synthesized as described elsewhere (Parzuchowski et al. 2007).

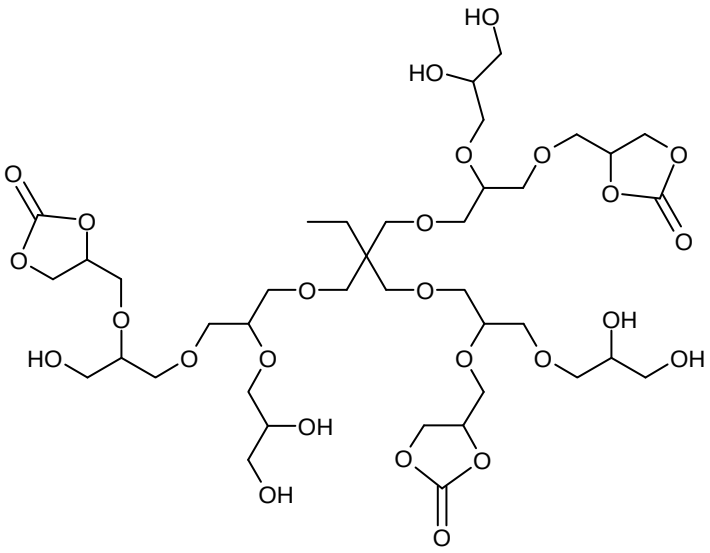

Fig. 1 Theoretical structure of HBP-1W

Dicarboxylic acids (Sigma-Aldrich): white or white-off solids of the melting points as shown in Table 1 were used.

Table 1. Melting point of the studied acids

acid	**melting point [°C]**
adipic	153
sebacic	132
succinic	187
phthalic	210 (dec.)
isophthalic	342
terephthalic	>300

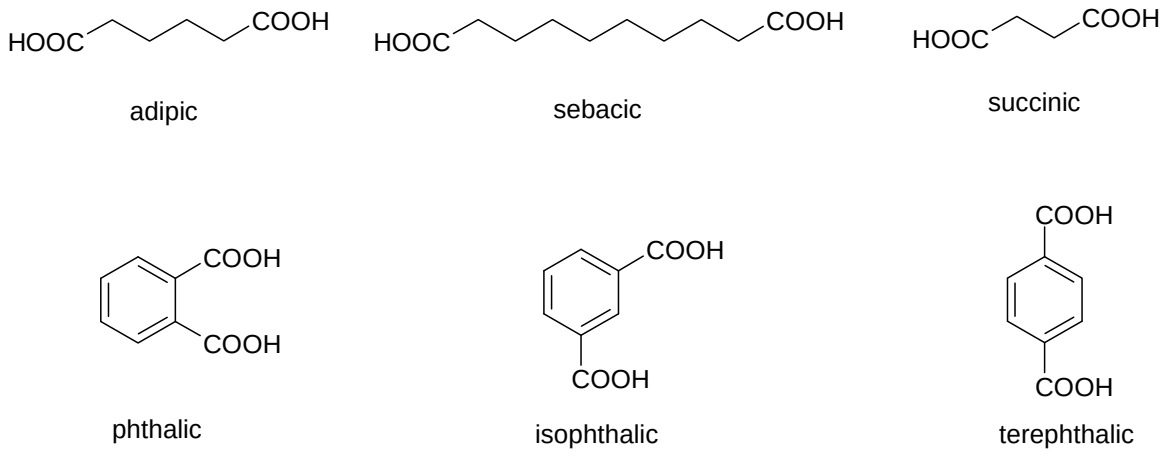

Fig. 2 Structures of the acids used in the experiments

Due to high viscosity of the polyglycerol, adhesive was formulated after preheating of HBP-1W to 60ºC and then carboxylic acid was added in 1:1 molar ratio. The components were thoroughly mixed for 5 min and then tin(II) 2-ethylhexanoate (5wt%) was added as catalyst and mixture was subjected to curing at 170ºC for 30 min.

RESULTS AND DISCUSSION

The results reported previously (Mamiński et at. 2011a,b) showed that bonding of wood samples was possible only for sebacic acid. The obtained dry shear strength of bond line made in solid beech was 1.9 N/mm^2, succinic acid ester exhibited dry shear strength of 1.0 N/mm^2. While the samples bonded with adipic acid ester and all three aromatic acids esters delaminated spontaneously, although ester formation in all cases was proved.
Those observations suggested that melting point of an acid is the factor that determines acid solubility/miscibility in the polyglycerol and, subsequently, affects resultant homogeneity of the system. Thus, it was found that 5-min mixing was an amount of time sufficient for achieving homogeneity only by the mixtures with aliphatic acids. All the series containing aromatic acids were inhomogeneous. The microphotographs of textures of the adhesive systems were shown in Figs. 3 and 4.

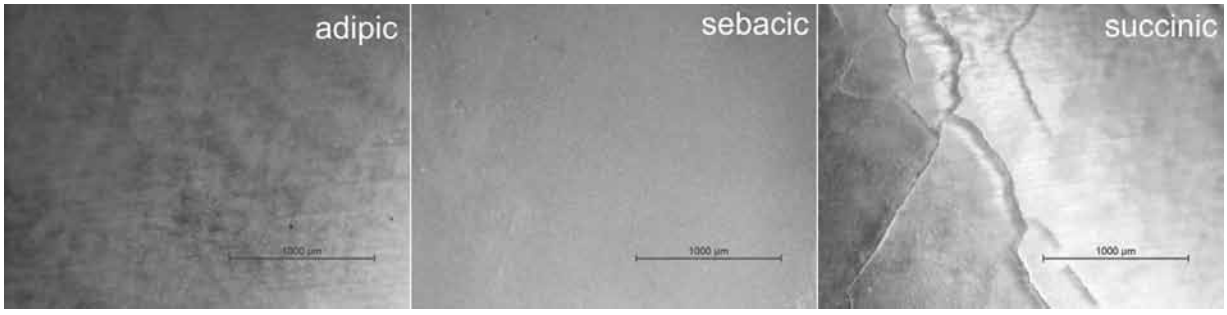

Fig. 3 Microphotographs of the polyesters of aliphatic dicarboxylic acids

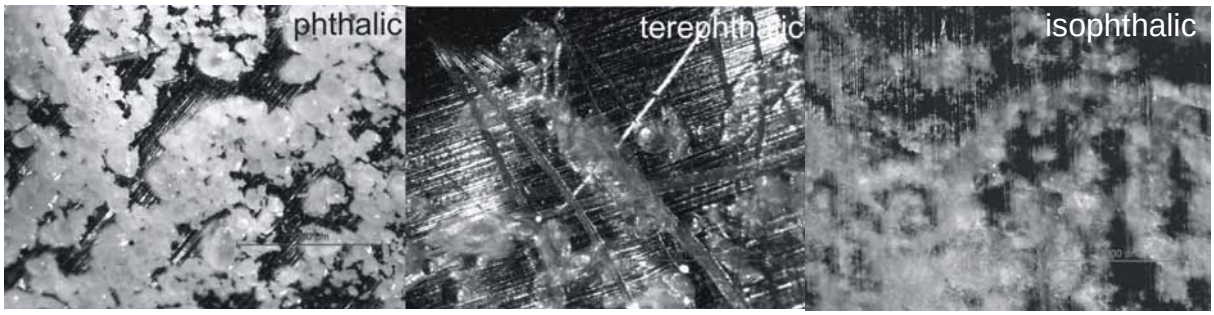

Fig. 4 Microphotographs of the polyesters of aromatic dicarboxylic acids

Now one can see that homogeneity was never achieved for the systems containing acids with high melting point (>200ºC): phthalic, isophthalic and terephthalic (Fig. 4). The phenomenon can be ascribed to immiscibility or insolubility of the acids in the polyglycerol. Temperature of mixing was too low for melting of the acid and achieving full homogeneity.

On the other hand, aliphatic acids with lower melting points (<200ºC) allowed for homogeneity of the mixture (Fig. 3) which confirms the assumptions on melting point as a key factor making efficient mixing and compounding of polyglycerol-dicarboxylic acid possible.

CONCLUSIONS

It was found that performance of 2-component adhesive systems based on a hyperbranched polyglycerol containing cyclic carbonates and dicarboxylic acid strongly depends on efficacy of mixing those two components which is governed by their miscibility and/or solubility. When mixing is performed at temperatures below 100ºC, homogeneity can be achieved only for the acids of low melting points. Thus, aromatic acids seem not to be applicable in 2-component polyester adhesives.

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Streszczenie: *Wpływ temperatury topnienia kwasu zastosowanego do estryfikacji silnie rozgałęzionego poliglicerolu na homogeniczność poliestru.* Silnie rozgałęziony poliglicerol zawierający ugrupowania cyklowęglanowe został poddany estryfikacji trzema dikarboksylowymi kwasami alifatycznymi i trzema aromatycznymi. Wykazano, że temperatura topnienia kwasu jest czynnikiem determinującym osiągnięcie homogeniczności przez układ. Przeprowadzono analizę mikrostruktury utwardzonych poliestrów.

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