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Imidazol-catalyzed esterification of hyperbranched polyglycerols containing terminal cyclic carbonate or hydroxyl groups – an approach to wood adhesives

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Abstract: *Imidazol-catalyzed esterification of hyperbranched polyglycerols containing terminal cyclic carbonate or hydroxyl groups – an approach to wood adhesives.* Imidazole-catalyzed esterifications of hyperbranched polyglycerols bearing cyclic carbonates or hydroxyl groups with phthalic anhydride were performed. FTIR spectra showed that imidazole – when compared to tin(II) 2-ethylhexanoate - provided higher yield of reaction in shorter time.

Keywords: hyperbranched polyglycerols, esterification, imidazole

INTRODUCTION

Schwenk et al. (1962) reported on reactivity of 5-member cyclic carbonates toward cyclic anhydrides with ester formation and elimination of CO_2 – as shown in Fig. 1. The main drawbacks of that approach are long time and high temperatures necessary for the reaction to complete. Transesterifications of cyclic carbonates with phthalic anhydride were studied by Berti et al. (1999). They found that the synthesis required temperature 250-300ºC, time 15-120 minutes and presence of Sn- or Ti-based catalysts.

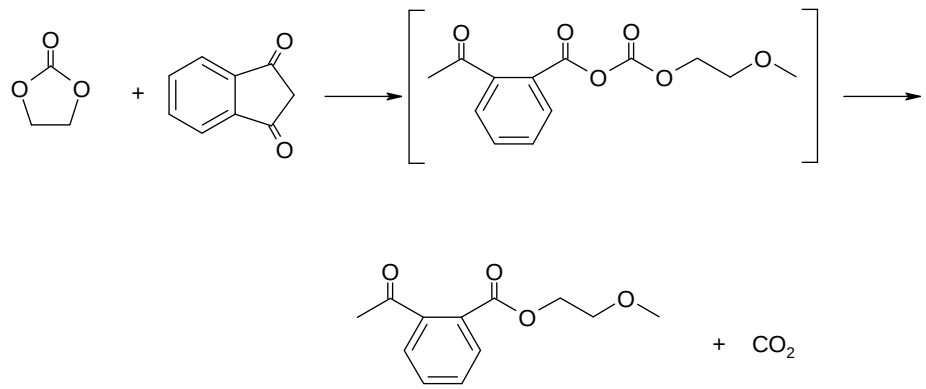

Fig. 1. Transesterification of 5-member cyclic carbonate with phthalic anhydride (from Rokicki 2000)

Most recently, Mamiński et al. (2011) described the results of investigations on 2-component polyester adhesives synthesized within a bond line from phthalic anhydride and hyperbranched polyglycerol bearing cyclic carbonates. It was shown that esterification required 30 min and temperature at least 150ºC when tin(II) 2-ethylhexanoate (5wt%) was used as a catalyst. Even at such severe conditions, substantial amount of carbonates remained unreacted.

Connors and Pandit (1978) discussed *N*-methylimidazole- and imidazole-catalysed esterification mechanisms involving cyclic anhydrides and hydroxy compounds. They reported high catalytic activity of imidazole. Therefore, this work regards an approach to wood adhesives based on *in situ* imidazole-catalysed esterification of a hyperbranched polyglycerols with phthalic anhydride.

MATERIALS AND METHODS

Hyperbranched polyglycerol Bis101: brown oil of viscosity 1800 Pa·s at 20ºC, theroretical molecular weight 969.1 g/mol. From size exclusion chromatography (SEC) M_n = 1533, M_w = 4504 and D = 2.94 were found. Structure shown in Fig. 2.
Hyperbranched polyglycerol HBP-1W bearing 3 cyclic carbonate groups – highly viscous (1300 Pa·s at 20ºC) dark yellow oil. Molecular weight 953 g/mol. Structure was shown in Fig. 3.

An aliquot of a polyglycerol was heated to 60ºC, then phthalic anhydride was added and mixed. HBP-1W : anhydride molar ratio was 1:3, while Bis101 : anhydride 1:12. After the components were thoroughly compounded, catalyst imidazole (5 wt%) was added. In order to investigate ester formation, the mixtures were subjected to curing at 170ºC for 15 minutes. Reaction progress was monitored by FTIR. Spectra of polyesters were recorded in KBr.

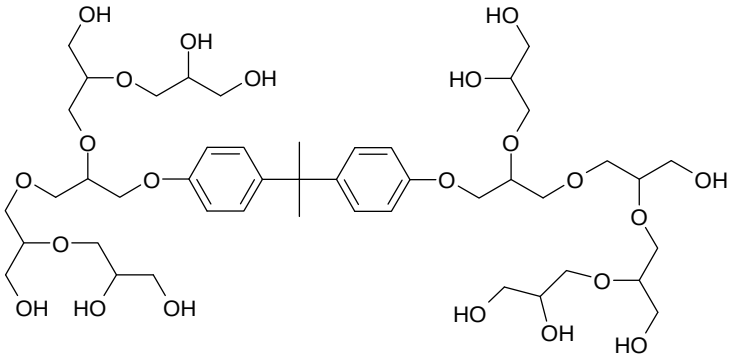

Fig. 2 Theoretical structure of polyglycerol Bis101

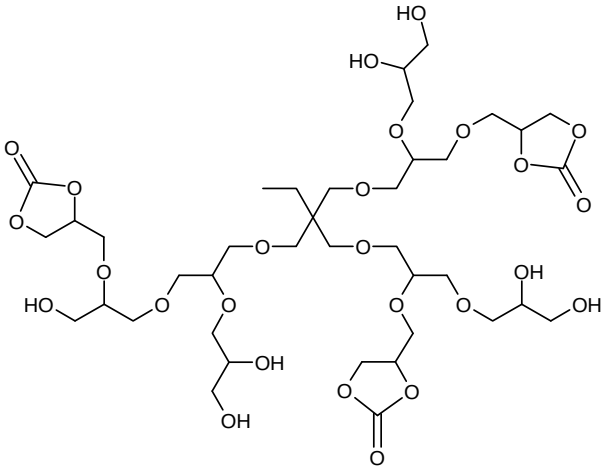

Fig. 3 Theoretical structure of HBP-1W

RESULTS AND DISCUSSION

FTIR spectra of both cured polyesters shown in Figs. 3 and 4 indicate strong ester C=O bands at *ca.* 1723 cm^{-1} which do not come from the anhydride since phthalic anhydride bands are as follows: (cm^{-1}) 3096, 3084, 3073, 1854, 1790, 1771, 1764, 1702, 1405, 1283, 1262.

The observations confirm assumptions that imidazole catalytic activity is higher than previously used tin(II) 2-ethylhexanoate, since 15-min esterification yielded substantial amount of the polyester. Moreover, 1791 cm^{-1} band (unreacted cyclic carbonate) (Fig. 3) is much weaker than the one for the analogue tin(II) 2-ethylhexanoate-catalysed system described previously (Mamiński et al. 2011).

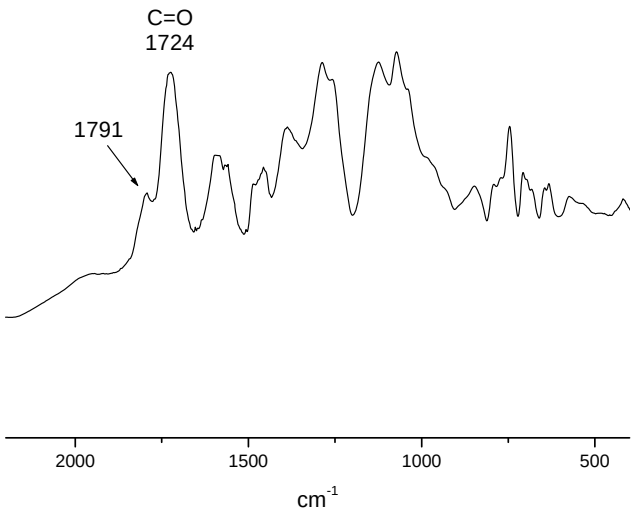

Fig. 3 FTIR spectrum of polyester from HBP-1W and phthalic anhydride cured at 170ºC for 15 min in the presence of imidazole as a catalyst

Thus, it was shown that the polyglycerols bearing either cyclic carbonates or hydroxyls could be successfully esterified with phthalic anhydride in reaction catalyzed by tin(II) 2-ethylhexanoate or imidazole. However, it is worth noting that the latter one provides more rapid reaction due to its high catalytic activity.

Unfortunately, bonding attempts performed in solid wood occurred unsuccessful, since specimens delaminated spontaneously, although ester was formed in the bond line.

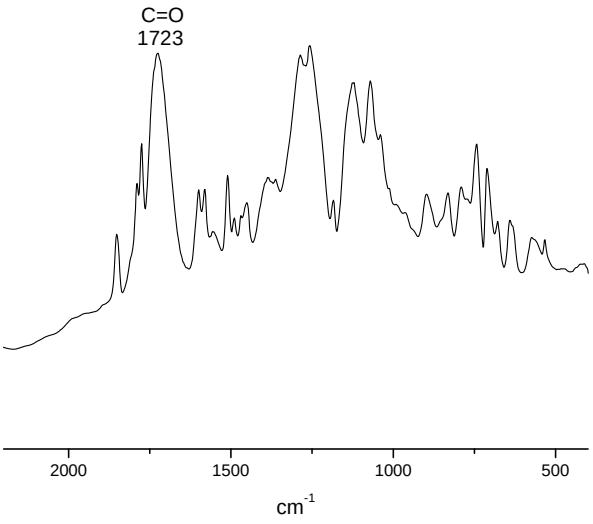

Fig. 4 FTIR spectrum of polyester Bis101 and phthalic anhydride cured at 170ºC for 15 min in the presence of imidazole as a catalyst

CONCLUSIONS

It was found that *in situ* esterification of hyperbranched polyglycerols in tin(II) 2-ethylhexanoate- or imidazole-catalyzed systems was possible, however formed polyester exhibited no bonding properties. Thus, the invesitigated 2-component adhesive systems are not applicable in wood bonding and polyester resin synthesis instead should be considered in future work.

ACKNOWLEDGMENTS

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Streszczenie: *Estryfikacja silnie rozgałęzionych poliglicerolі zawierających terminalne grupy cyklowęglanowe lub hydroksylowe – wykorzystanie w klejach do drewna***.** Przeprowadzono estryfikację silnie rozgałęzionych poliglicerolі zawierających terminalne grupy cyklowęglanowe lub hydroksylowe bezwodnikiem ftalowym w układzie katalizowanym imidazolem. Na podstawie widm FTIR wykazano, że katalizator ten, w porównaniu do dibutylodilaurynianiu cyny, umożliwia skrócenie czasu reakcji.

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