EFFECTS OF ADDITIVES ON PALM-BASED POLYURETHANE FOAMS

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ABSTRACT

A preliminary study was made on the effects of some additives on the properties of palm-based polyurethane foam, such as density, hardness and curing time. The additives - Ethacure 100, Ethacure 300, Amisol CDE and KD-1, N-methyl-2,2′-iminodiethanol (MDEA) and phthalic anhydride - were incorporated into the polyurethane foam by mixing with blended polyols (40 g palm-based polyol with 60 g petro-based polyol) and MDI (4,4′-diphenylmethane diisocyanates), and 2.3 g water used as the blowing agent. Incorporating 5 ppH Ethacure 100 and 10 ppH Amisol (either CDE or KD-1) substantially increased the density of the foams from 264 kg m^{-3} to 398.28 kg m^{-3} and the hardness from 34.5 to 55 shore D, while the demoulding time was decreased from 20 min to less than 5 min.

Keywords: polyurethane foams, polyols, additives.

INTRODUCTION

About 90% of the polyols used for the production of polyurethane (PU) foam worldwide are based on polyethers derived from ethylene or propylene oxides. However, there is increasing interest to use renewable raw materials, like vegetable oils/fats, instead due to the depletion of petroleum (Siwayanan *et al*., 1999).

Since the 1960s, sugar and its derivatives have been used to produce polyols, especially for rigid PU foam. A refrigerated container panel made from castor oil PU foam was comparable in cost and properties to the conventional material (Reed, 1997). Dahlke *et al.* (1997) and Heidbreder *et al.* (1999) also found the properties of vegetable oil PU systems to be comparable to those of standard polyether systems. Their polyols were made by ring-opening addition of ethylene glycol to epoxidize soya, rapeseed, castor or sunflower oils. The polyols showed good compatibility with aromatic isocyanates.

In Malaysia, the Malaysian Palm Oil Board (MPOB) first produced polyol from epoxidized palm oil in the late eighties (Hassan *et al*., 1993), and today a pilot plant capable of producing 500 kg batches of palm polyols has been commissioned. The polyols are suitable for rigid, semi-rigid and flexible PUs for various uses. Additives are important in conferring different properties to PU. In this paper, the effects of some of these - Ethacure 100, Ethacure 300, Amisol CDE and KD-1, N-methyl-2,2′-iminodiethanol and phthalic anhydride - on the density, hardness and curing of palm-based PU foam are investigated.

EXPERIMENTAL

Materials

A palm-based polyol was produced by a MPOB/InterMed patented process (patent Singapore No: 9610425-2, patent application/Malaysia: PI 9502302 and patent application/Indonesia: P 962884),

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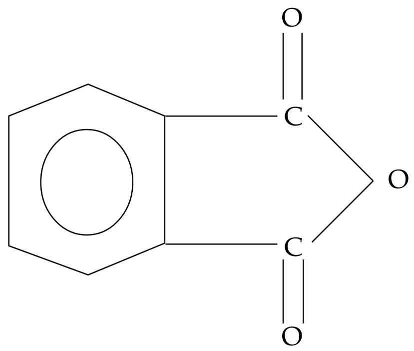
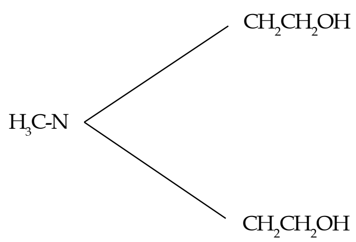
polyether polyol (SU-464) was obtained from Mitsui Toatsu Chemicals, crude MDI (4,4′-diphenylmethane diisocyanate) from Dow Chemicals, Niax A33 (amine catalyst) and L6900 (surfactant) from Osi Specialties, dibutyltin dilaurate (DD) (tin catalyst) from Machwolk Sdn. Bhd., diethanolamine (DEA) and triethanolamine (TEA) (cross-linker) from BASF (Malaysia), Ethacure 100 and Ethacure 300 from Albemarle, Amisol CDE and KD-1 (both of which confer similar properties to PU foam) from K & FS Pte. Ltd., and phthalic anhydride (PA) and N-methyl-2,2′-iminodiethanol (MDEA) from Merck-Schuchardt. Water was used as the blowing agent. Shown below are the structures of phthalic anhydride and N-methyl-2, 2′-iminodiethanol (MDEA).



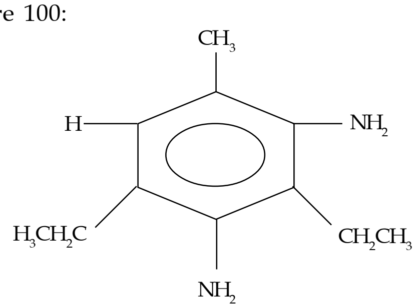
Phthalic anhydride



MDEA

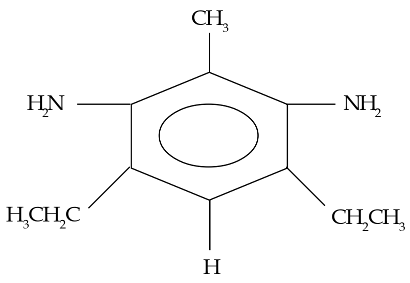
Ethacure 100 (DETDA) comprises two isomers of diethyltoluenediamine and Ethacure 300 (DMTDA) two isomers of benzenediamine-bis(methylthio)-. Their structures are given below:

Ethacure 100:



97.5%

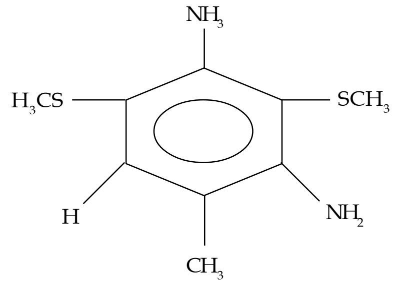
2,4-diethyltoluene-1,3-diamine



2.5%

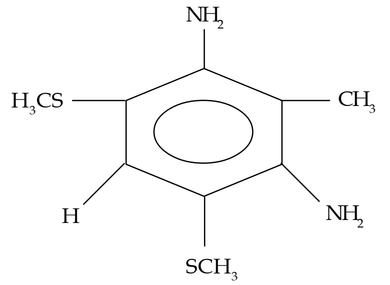
2,4-diethyltoluene-1,5-diamine

Ethacure 300:



80%

1,3-benzenediamine-4-methyl -2,6-bis (methylthio)-



20%

1,3-benzenediamine-2-methyl 1-4,6-(methylthio)-

Method: Foam Preparation

MDI (165 g to 195 g) was added to a mixture containing polyols (60 g petro-based polyether polyol and 40 g palm-based polyol), additives (as shown in *Table 1*) and distilled water (2.3 g), followed by vigorous stirring at 1100 rpm. When the mixture was about to gell, it was quickly poured into a mould (18.9 cm ∞ 9.8 cm ∞ 1.0 cm). After 5 - 10 min, depending on how fast the foam became tack free, it was removed from the mould.

Measurement of Density

The specimens were weighed and measured, and their density in kg m^{-3} calculated.

TABLE 1. ADDITIVES TO FOAMS

Additive	Amount, g
L6900	2
A33	2
DEA	5
TEA	1
DD	0.5
Amisol CDE or KD-1	Variable (2 g, 5 g, 10 g and 15 g)
Ethacure 100	Variable (2 g, 5 g, 10 g and 15 g)
Ethacure 300	5 g (used with variable amounts of MDI)
PA	Variable (0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g)
MDEA	Variable (0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g)

Measurement of Hardness

The hardness of the foams was measured at ambient temperature using a Durometer, ASTM D2240, shore instrument (Instron) in shore D units.

RESULTS AND DISCUSSION

Effect of MDI Concentration on Density and Hardness

The amount of MDI was varied from 165 g to 195 g for 100 g polyol. Three formulations were made, *i.e.* without Ethacure, with Ethacure 100 (5 ppH, or parts per hundred) and with Ethacure 300 (5 ppH), all with the same amount (10 ppH) of Amisol CDE.

With or without Ethacure 100, the density of the foam decreased with MDI whereas with Ethacure 300, the maximum density was obtained with 185 ppH MDI (*Figure 1*). The increase in density by Ethacure 300 was due to its extra functional groups ($-SCH_3$) available for cross-linking.

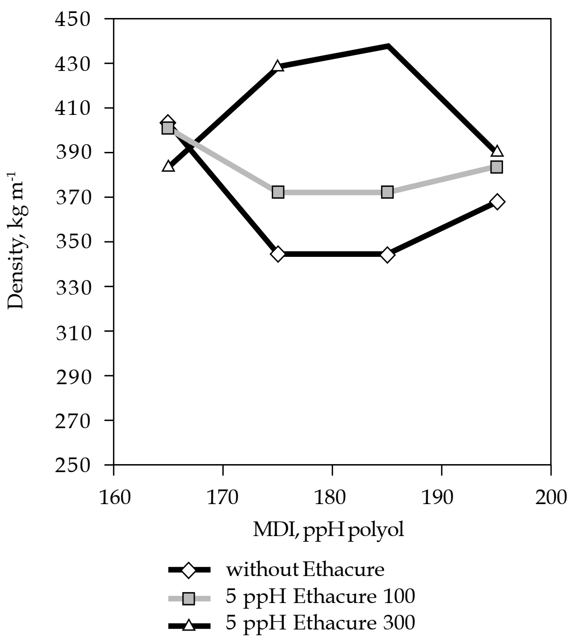


Figure 1. Effect of MDI concentration on density of palm-based PU foam.

Figure 2 shows that the hardness decreased with MDI concentration. With Ethacure 300, the hardness increased slightly initially but then decreased after 175 ppH MDI. As 165 ppH MDI gave generally the best density and hardness, it was used for the rest of the study. Ethacure 300 was not investigated further as its foam was less hard than that with Ethacure 100.

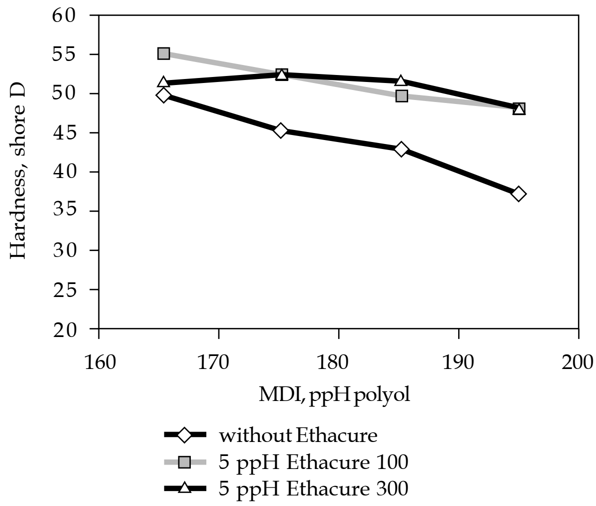


Figure 2. Effect of MDI concentration on hardness of palm-based PU foam.

Effect of Amisol KD-1 Concentration on Density and Hardness

Figure 3 shows that with Ethacure 100, the density of the PU foam decreased with the Amisol content. The converse was true without Ethacure 100 although the density was fairly constant from 5 ppH to 15 ppH. The density without Ethacure 100 was lower than with Ethacure 100 except at the highest level of Amisol (15 ppH) where they were similar.

The hardness of the foam increased with the Amisol content until 10 ppH and then decreased

(*Figure 4*), possibly due to the high viscosity caused by excess Amisol which resulted in poor homogeneity of the mixture. Without Ethacure 100, the foam was not as hard as with Ethacure. Amisol improved the foam properties by its high (95%) amine content. During foaming, the amine group reacts with isocyanate to form substituted urea, which, in turn, reacts with another isocyanate to produce a biuret link in one of the main reactions leading to branching and cross-linking. *Figures 5* and *6* show the effect of Amisol on the PU foam structure with/without Ethacure 100, respectively.

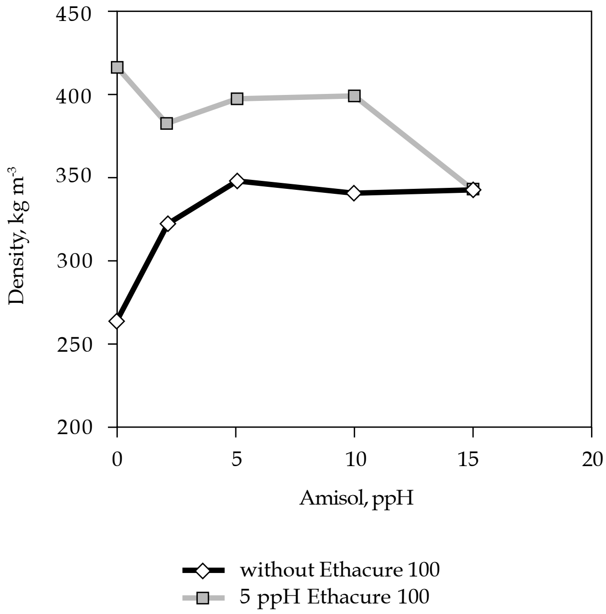


Figure 3. Effect of Amisol KD-1 concentration on density of palm-based PU foam.

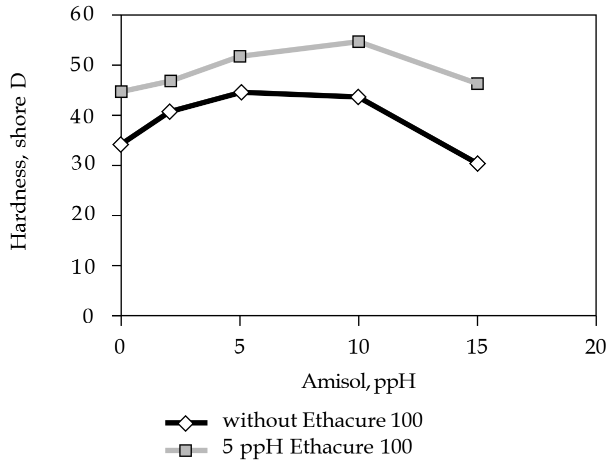


Figure 4. Effect of Amisol KD-1 concentration on hardness of palm-based PU foam.

Both the foams in *Figure 5* had a fine cell structure, but the density was lower with Amisol (344.62 kg m^{-3}) than without (415.42 kg m^{-3}) in the presence of 5 ppH Ethacure 100. Both foams had similar hardness - 46.6 shore D and 45.2 shore D, respectively.

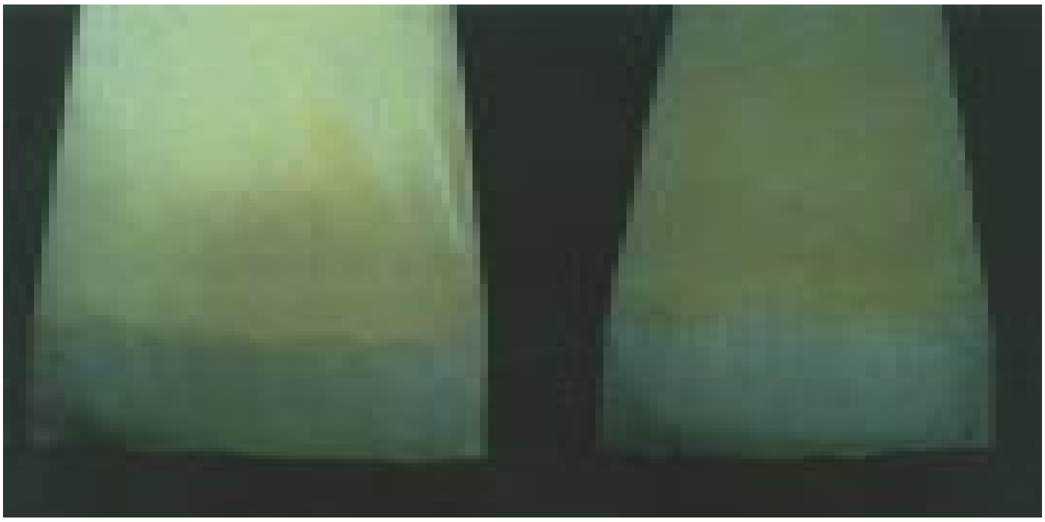
Without Amisol, the foam density was lower (264 kg m^{-3}) than with it (343.7 kg m^{-3}). However, Amisol decreased the hardness from 34.9 shore D to 30.9 shore D. The cell structure of the foam without Amisol was better in terms of cell size (smaller) as compared to with Amisol (*Figure 6*).

Effect of Ethacure 100 Concentration on Density and Hardness

Figure 7 shows that with/without Amisol KD-1, the density of the foams increased with the Ethacure

a. Without Amisol. b. 15 ppH Amisol.

Figure 5. Effect of Amisol KD-1 on the structure of PU foam with 5 ppH Ethacure 100.



a. Without Amisol. b. 15 ppH Amisol.

Figure 6. Effect of Amisol KD-1 on PU foam structure.

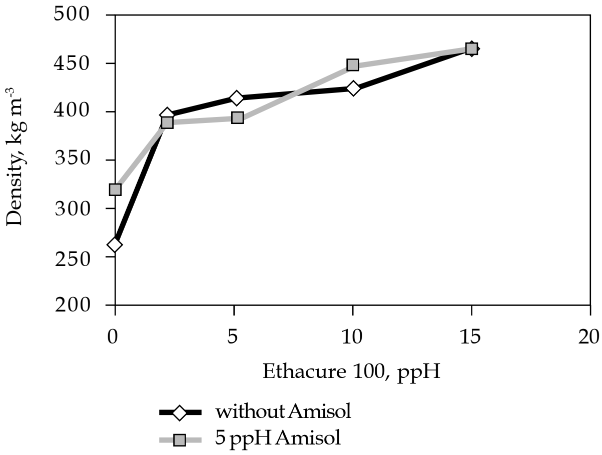


Figure 7. Effect of Ethacure 100 concentration on density of palm-based PU foam in the presence of Amisol KD-1.

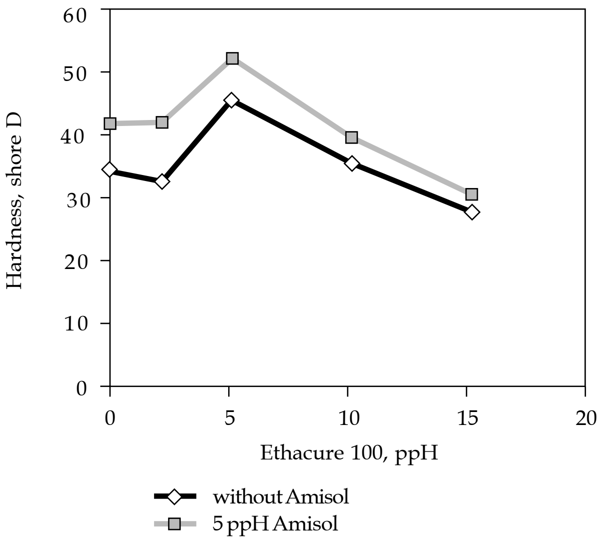


Figure 8. Effect of Ethacure 100 concentration on hardness of palm-based PU foam in the presence of Amisol KD-1.

100 concentration. The densities of both the foams were similar. With/without Amisol, the hardness increased only up to 5 ppH Ethacure 100, and then decreased. Without Amisol, the hardness was lower (*Figure 8*).

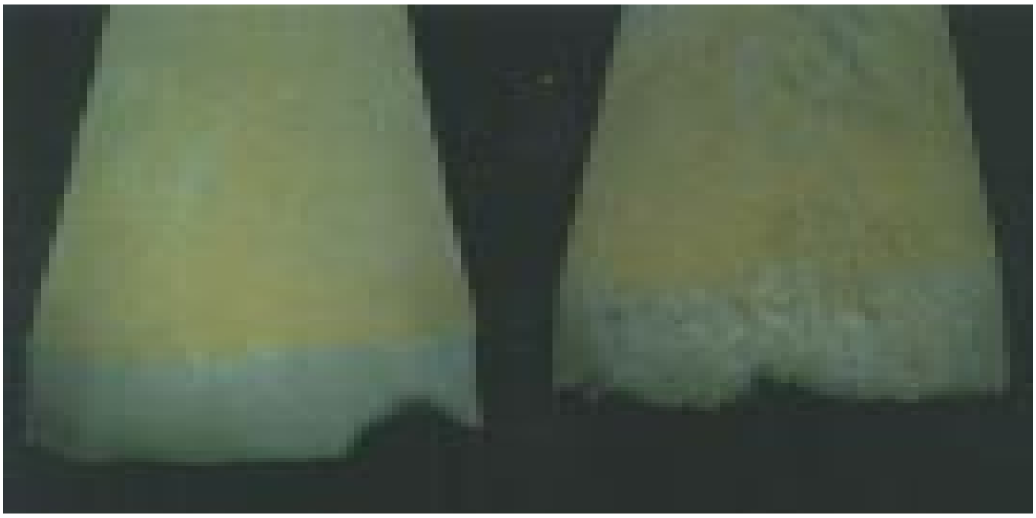
Ethacure 100 and 300 are chain extenders, which shorten the curing time and increase the foam hardness. With their rapid and vigorous reaction with the isocyanate groups, not only did the polymers set quickly but branching points were formed by the biuret linkages. Furthermore, cyclic extenders, which the Ethacures are, confer greater foam strength than linear extenders (Wirpsza, 1993).

However, with •10 ppH Ethacure 100, the mixture became too viscous and could not mix well, and was slow in rising. The excess Ethacure 100 did not allow sufficient time for the necessary chemical reactions to happen before the foam hardened. Therefore, the foam was coarse and its hardness uneven.

With/without Amisol and •10 ppH Ethacure 100, it took >20 min for the foam to demould. ***Figures 9*** and *10* show the effect of Ethacure 100 on the structure of PU foam without/with Amisol, respectively.

With 5 ppH Ethacure 100, a fine cell structure was formed with a density of 415.42 kg m^{-3} and a hardness of 45.2 shore D. The higher concentration produced a coarser cell structure with a higher density of 467.44 kg m^{-3} and a lower hardness of 28 shore D (*Figure 9*).

With Amisol, 5 ppH Ethacure 100 produced a better foam than 15 ppH Ethacure 100 **-** harder (52.1 *vs.* 30.5 shore D) but less dense (396.12 kg m^{-3} *vs.* 466.31 kg m^{-3}) (*Figure 10*).



a. 5 ppH Ethacure 100. b. 15 ppH Ethacure 100.

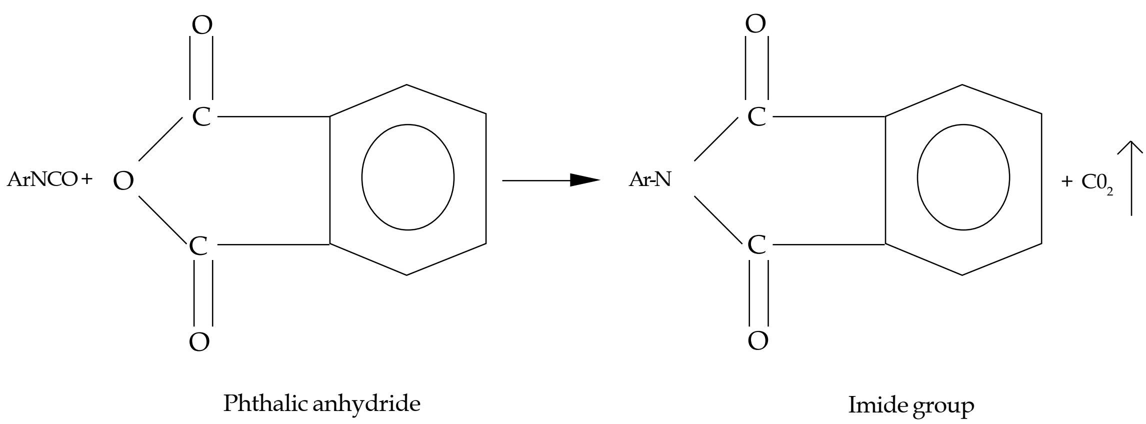
Figure 9. Effect of Ethacure 100 concentration on the structure of PU foam without Amisol KD-1.

a. 5 ppH Ethacure 100. b. 15 ppH Ethacure 100.

Figure 10. Effect of Ethacure 100 concentration on the structure of PU foam with 5 ppH Amisol KD-1.

Effects of Phthalic Anhydride and MDEA

Effect of phthalic anhydride concentration. Phthalic anhydride was added from 0.5 to 2.5 ppH with/without MDEA at 1.0 ppH. The densest foam was produced with 1.5 ppH phthalic anhydride (*Figure 11*). Without MDEA, the density was higher than with MDEA. The acid anhydride reacts with isocyanate with evolution of CO_2 to yield an imide group. With low phthalic anhydride, the CO_2



released was insufficient to generate the necessary foam structure, but more phthalic anhydride would released more CO_2 resulting in a more *bubbly* foam of lower density.

A similar trend was observed for hardness which also peaked at 1.5 ppH phthalic anhydride (*Figure 12*). Excess phthalic anhydride increased the gelling and rising time resulting in a longer demoulding time. *Figures 13* and *14* show the effect of phthalic anhydride on the structure of PU foam with 5 ppH Ethacure 100 and 10 ppH Amisol KD-1 without/with MDEA, respectively.

Both the foams showed a fine cell structure (*Figure 13*) despite the high densities - 473.6 kg m^{-3} with 1.5 ppH and 430.08 kg m^{-3} with 2.5 ppH phthalic anhydride. The hardness of the foams was similar - 53.6 and 51.5 shore D for the two concentrations, respectively.

The cell structures of both foams were similar (*Figure 14*). The density with 1.5 ppH phthalic anhydride was slightly higher than with 2.5 ppH phthalic anhydride - 459.02 kg m^{-3} *vs.* 406.49 kg m^{-3}. The foam with 1.5 ppH phthalic anhydride (54 shore D) was also harder than that with 2.5 ppH phthalic anhydride (49.5 shore D).

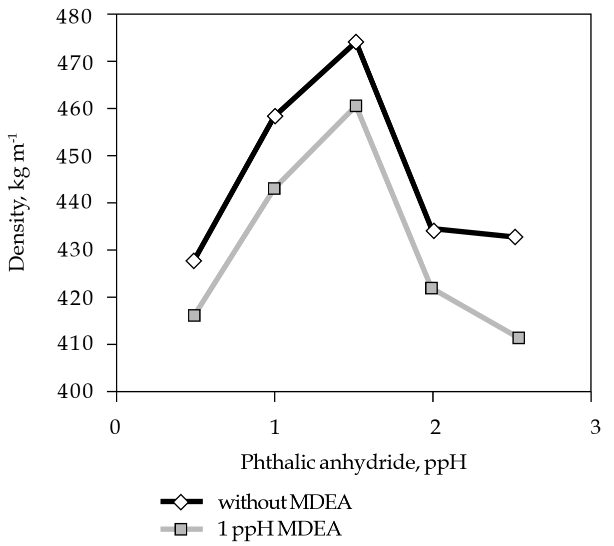


Figure 11. Effect of phthalic anhydride concentration and MDEA on density of palm-based PU foam.

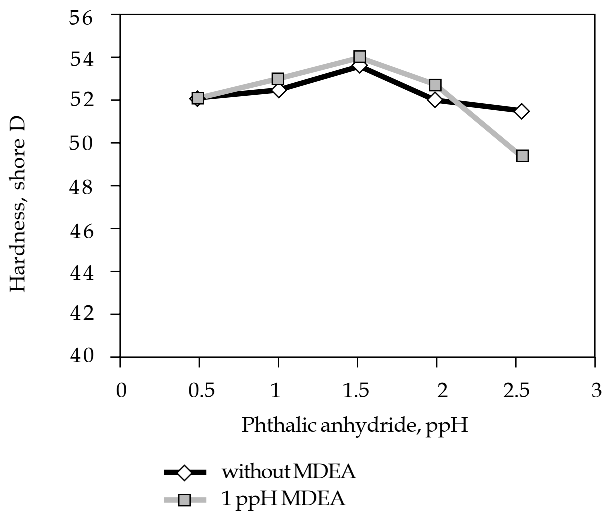
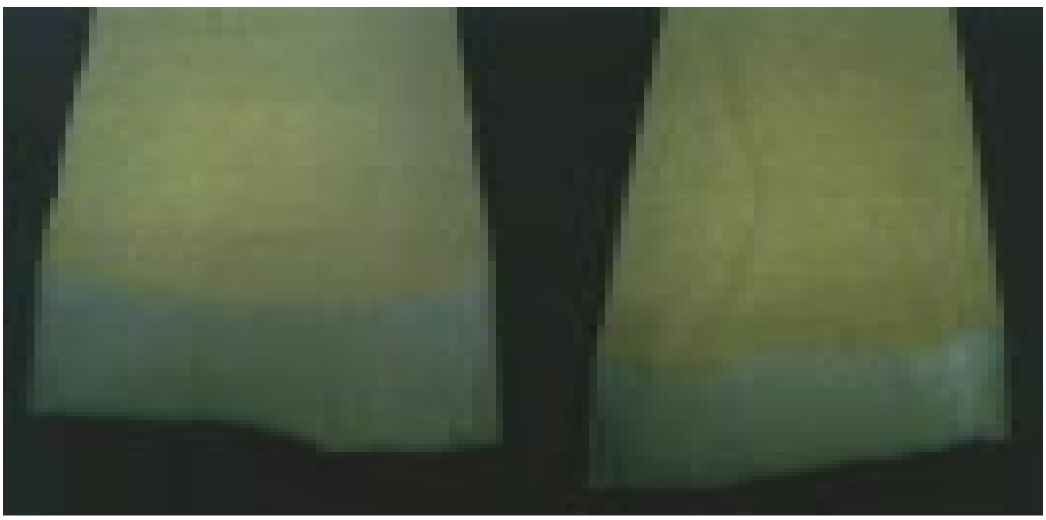


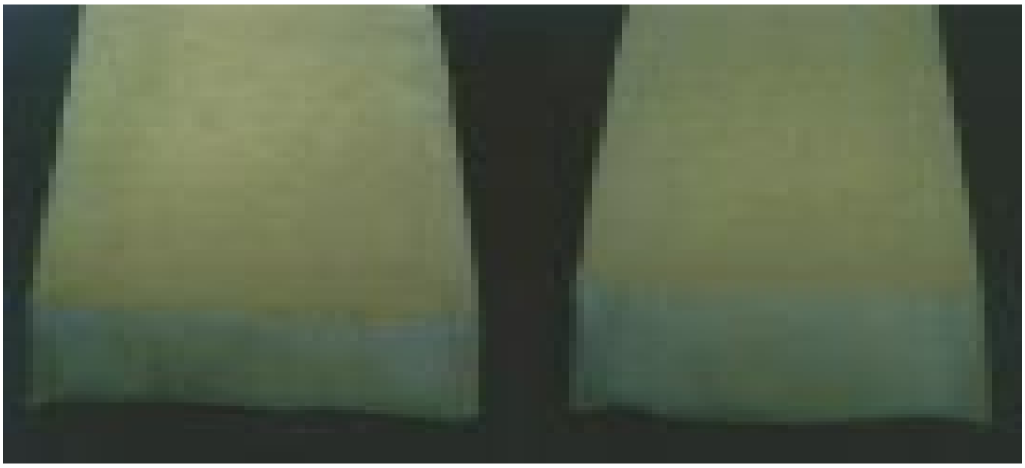
Figure 12. Effect of phthalic anhydride concentration and MDEA on hardness of palm-based PU foam.



a. 1.5 ppH phthalic anhydride.

b. 2.5 ppH phthalic anhydride.

Figure 13. Effect of phthalic anhydride concentration on the structure of PU foam with 5 ppH Ethacure 100 and 10 ppH Amisol KD-1.



a. 1.5 ppH phthalic anhydride. b. 2.5 ppH phthalic anhydride.

Figure 14. Effect of phthalic anhydride concentration on the structure of PU foam with 5 ppH Ethacure 100, 10 ppH Amisol KD-1 and 1 ppH MDEA.

Effect of MDEA Concentration. MDEA was added from 0.5 to 2.5 ppH with/without phthalic anhydride at 1.0 ppH. The foam density peaked at 1.0 ppH MDEA (*Figure 15*). The foam without phthalic anhydride was less dense than that with phthalic anhydride except with 0.5 ppH MDEA.

Figure 16 shows that the hardness of both the foams (without/with phthalic anhydride) decreased with the MDEA concentration. The foam with phthalic anhydride was harder than that without.

Thus, phthalic anhydride increased the foam density but had little effect on the hardness, while MDEA had little effect on either.

CONCLUSION

Polyols, isocyanates and water react to form PU foam. For different applications, PU of different characteristics are required. Adding 5 ppH Ethacure 100 and 10 ppH Amisol (either CDE or KD-1) significantly increased the density (398.28 kg m^{-3} *vs*. 264 kg m^{-3}) and hardness (55 shore D *vs*. 34.5 shore D) from the foams without the additives, while the demoulding time was shortened to less than 5 min.

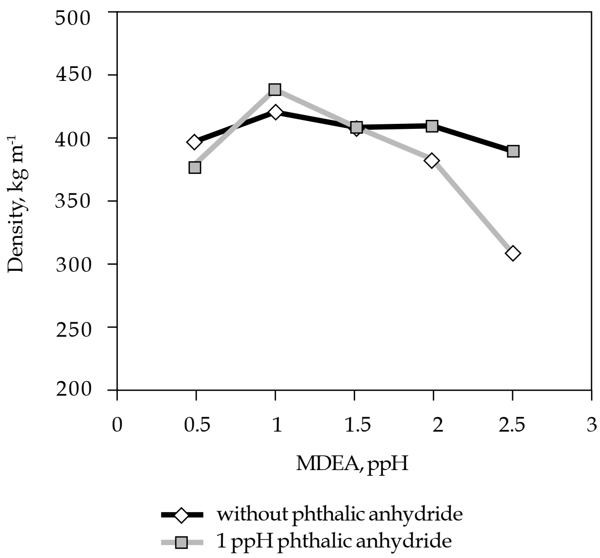


Figure 15. Effect of MDEA concentration and phthalic anhydride on density of palm-based PU foam.

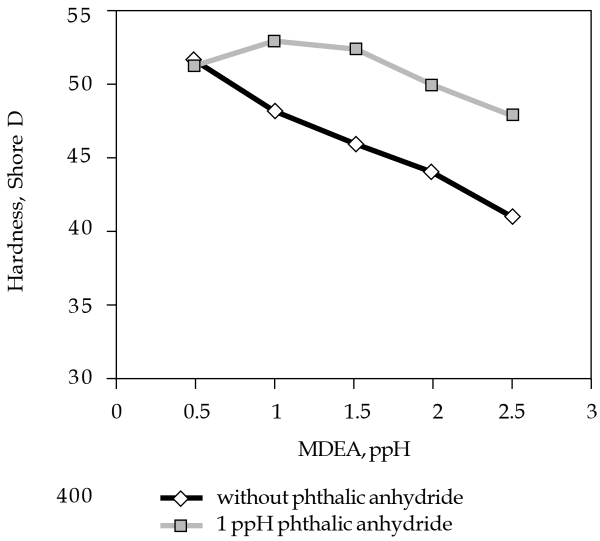


Figure 16. Effect of MDEA concentration and phthalic anhydride on hardness of palm-based PU foam.

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