The Effect of Triethylene Diamine on the Properties of Waste Paper Foam Composites

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Abstract: *The effect of triethylene diamine (TEDA) as a catalyst and waste paper filler content on the properties of waste paper foam composites was investigated. The results indicate that an increase of waste paper filler content leads to an increased compressive strength, elastic modulus and hardness. At constant waste paper content, foam composites produced using the TEDA catalyst result in higher values of hardness, compressive strength and elastic modulus compared to the waste paper foams produced without the aid of the catalyst.*

Keywords: waste paper, polyurethane foam, catalyst, composites

Abstrak: *Kesan trietilena diamina (TEDA) sebagai pemangkin dan pembebanan yang berbeza daripada sisa kertas ke atas sifat-sifat komposit busa kertas telah dikaji. Keputusan menunjukkan dengan semakin meningkatnya kandungan sisa kertas, maka kekuatan mampatan, modulus elastik dan kekerasan meningkat. Pada kandungan sisa kertas yang sama, komposit busa pemangkin menunjukkan nilai yang lebih tinggi terhadap kekerasan, kekuatan mampatan dan modulus elastik dibandingkan busa sisa kertas tanpa pemangkin.*

Kata kunci: sisa kertas, busa poliuretena, pemangkin, komposit

1.   INTRODUCTION

Polyurethane foams are produced by the reaction of polyisocyanate, polyol and water in the presence of a catalyst and other auxiliary agents. The polyurethane foam formation reaction essentially consists of a urethane reaction (gelling) and urea reaction (blowing) accompanied by the generation of CO_2. However, many complex reactions occur during the formation of a polyurethane foam. Catalysts play an important role in the control and balance between the gelling and blowing reactions. In addition to primary reactions, the catalytic activity of cross-linking reactions such as allophanate, biuret and isocyanurate formation are considered to have an effect on both the foaming behaviour and the foam properties. It is therefore important to better understand these cross-linking activities for the design of novel catalyst systems.[1–7] The reactions of isocyanates,

especially the aliphatic isocyanates, with the hydroxyl group of water are relatively slow at ambient temperature in the presence of a catalyst. Organo-metallic compounds or tertiary amines are normally needed to catalyse the cross-linking of the isocyanates with the hydroxyl groups at ambient conditions.[8–9] In this paper, the effects of TEDA on the properties of waste paper foam composites are reported.

2.   EXPERIMENTAL

Polyethylene glycol (PEG) 400 and the catalyst 1,4-Diazabicyclo [2.2.2] octan purum, also known as TEDA, were supplied by Fluka Chemie in Belgium and Diphenylmethane 4,4'-diisocyanate (MDI) (a mixture of di- and tri-isocyanates) for synthesis was obtained from Merck Schuchardt OHG in Germany. The typical density value of MDI is 1.239–1.241 g cm^{-3}. Three types of waste paper fillers were used in this research: paper sludge (PS), office white paper (OWP) and old newspaper (ONP). PS, a waste product from Premier tissue paper manufacturing, was obtained from Nibong Tebal Paper Mill Sdn. Bhd in Penang, Malaysia. The PS was dried in an oven at 80°C for 24 h to eliminate moisture and was then ground into powder form. An Endecotts sieve was used to obtain an average filler size of 63 µm (a density of 2.2 g cm^{-3}). The organic and inorganic contents of the PS were 59% and 41%, respectively. A similar process was used for the OWP and ONP fillers; however, they were first cut into small pieces and then soaked in a 10% sodium hydroxide solution. The organic content of the ONP was 89.6% while the inorganic content was 10.4%. Meanwhile, the organic and inorganic contents of the OWP were 86.9% and 13.1%, respectively. Table 1 shows the composition of the waste paper foams. Tables 2, 3 and 4 show the semi-quantitative compositional analysis of the PS, OWP and ONP.

2.1   Mixing Procedure

Waste paper foams were prepared using a 1:2 ratio of MDI to PEG and varying waste paper contents of 0, 10, 20, 30 and 40 wt. % via a direct reaction with diisocyanate. Three drops of water were then added as the blowing agent, and the combination was rapidly stirred (WiseStir DAIHAN scientific HS-30D) and then set to 400 rpm until it became warm. The mixture was immediately poured into a box and was left to equilibrate to room temperature. The resultant foams were allowed to cure at room temperature for one hour before being removed from the box.

Table 1: Composition of waste paper foams.

Materials	Waste Paper Foam				
MDI + PEG (% v/v)	100	90	80	70	60
Waste Paper (wt %)	0	10	20	30	40

Table 2: Semi-quantitative compositional analysis of PS using X-Ray Fluorescence Spectrometer Rigaku RIX 3000.

Component	Wt (%)
Na_2O	0.057
MgO	3.0
Al_2O_3	7.1
SiO_2	10.0
P_2O_5	0.065
SO_3	0.14
Cl_2O	0.19
K_2O	0.035
CaO	20.0
TiO_2	0.11
MnO	0.018
Fe_2O_3	0.19
ZnO	0.017
SrO	0.011
LOI (organic)	59.0

Note: LOI – Loss of Ignition

Table 3: Semi-quantitative compositional analysis of OWP using X-Ray Fluorescence Spectrometer Rigaku RIX 3000.

Component	Wt (%)
Na_2O	0.15
MgO	0.85
Al_2O_3	0.56
SiO_2	1.8
K_2O	0.02
CaO	8.9
TiO_2	0.03
MnO	0.03
Fe_2O_3	0.66
CuO	0.07
SrO	0.04
LOI (organic)	86.9

Note: LOI – Loss of Ignition

Table 4: Semi-quantitative compositional analysis of ONP using X-Ray Fluorescence
Spectrometer Rigaku RIX 3000.

Component	Wt (%)
Na_2O	0.78
MgO	0.44
Al_2O_3	2.4
SiO_2	2.0
K_2O	0.69
CaO	2.8
TiO_2	0.31
MnO	0.04
Fe_2O_3	0.8
CuO	0.07
ZnO	0.01
SrO	0.03
ZrO	0.02
BaO	0.06
LOI (organic)	89.6

Note: LOI – Loss of Ignition

2.2   Compression Test

The mechanical properties of the foams were measured according to
ASTM D695 using an Instron Machine 3366. A piece of foam (12.7 x 12.7 x
25.4 mm) was compressed between two flat plates at a cross-head speed of
5 mm min^{-1} until the specimen reached 70% of its original thickness. The test
was performed at $25 \pm 3 °C$. Five samples used and each composition has been
repeated two times.

2.3   Hardness Test

The Tecklock FO GS-710G durometer was selected for the hardness
measurements since it is specifically designed for testing relatively soft materials,
which includes the softness range of the foams. Its measuring concept is different
from standard durometers in that it is placed on the top of the specimen so that
the applied load in the test is its own weight and the dial reading indicates how
far the probe has been pushed back into the durometer body by the stiffness of
the material under test. The measurements of softness were made according to the
standard measuring procedures for durometers, ASTM D2240-03.[10] The
specimens had, as required, a minimum size of 50 mm × 50 mm with a thickness

in the range of 25–30 mm. The softness measurements were taken at six different locations. The maximum readings were recorded with the aid of the peak pointer of the durometer, which indicates the maximum indentation reading during the measuring period.

3.   RESULTS AND DISCUSSION

TEDA was used as the catalyst in the production of waste paper foam. The differences in the liquefaction behaviour of the waste paper are due to their different chemical compositions. The compressive strength results for waste paper foam with and without the catalyst are shown in Table 5. Figure 1 demonstrates the effect of filler content of the PS foam with and without the presence of the catalyst on the resulting compressive strength, and Tables 2, 3 and 4 present the chemical composition of the organic and inorganic components of the waste paper. The addition of fillers, which serve to reinforce the foam, significantly increased the value of the compressive strength. The inorganic entities are proposed to be present in smaller domains, where the inorganic molecules are less packed and cross-linked. The important function of the fillers are their organic content since the cellulose content acts as the source of polyhydric alcohol, which can react with polyurethane (PU) to make the foam more rigid. Therefore, the lower organic content of PS leads to its decreased rigidity as compared to OWP and ONP, with higher organic contents. In addition, the waste paper foams produced in the presence of the catalyst show a higher compressive strength compared to those produced without the aid of the catalyst, indicating that the catalyst plays an important role in modifying the mechanical properties of the foam. ONP foam showed to has high value of compressive strength compared to the ONP and PS foams as it contains higher cellulose contents, which is the sources of polyhydric alcohol and make the foam more rigid.

Table 5: Compressive strength of waste paper foam produced with and without the TEDA catalyst.

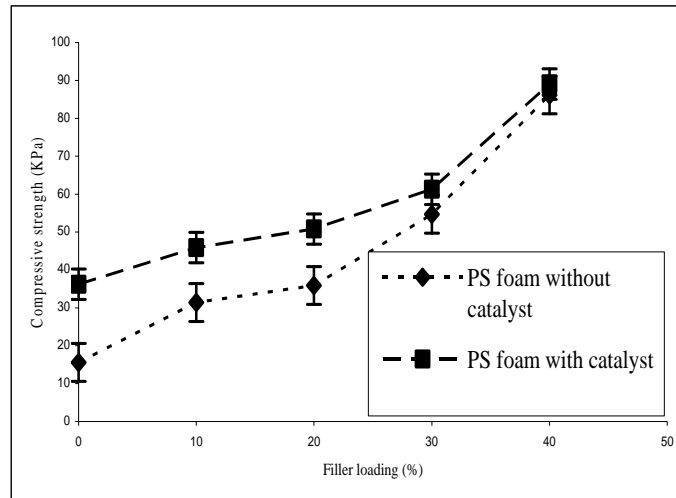| Filler loading (%) | Compressive Strength (KPa) | | | | | |
| | Without Catalyst | | | With Catalyst | | |
	PS foam	OWP foam	ONP foam	PS foam	OWP foam	ONP foam
0	15.6	15.6	15.6	36.22	36.22	36.22
10	31.4	38.6	48.1	45.9	48.5	50.62
20	35.9	57.4	71.9	50.8	60.41	73.9
30	54.7	66.8	100.5	61.3	68.07	104.76
40	86.2	103.2	115.3	89.05	115.02	120.6

Figure 1: The effect of filler content on the compressive strength of PS foam produced with and without the TEDA catalyst.

Table 6 presents the elastic modulus of waste paper foam produced with and without the TEDA catalyst as a function of filler contents. The effect of filler content on the elastic modulus of PS foam produced with and without the catalyst is shown in Figure 2. This plot clearly indicates that the elastic modulus of all of the PS waste paper foam increased with increasing waste paper content. This is because the addition of waste paper, which contains both organic and inorganic components, improves the stiffness of the foam. The PS foams produced using the TEDA catalyst exhibit higher elastic moduli compared to the PS foams produced without the catalyst. It can be seen that the ONP foam exhibits the highest elastic modulus, followed by the OWP and then the PS foams. The results also indicate that all of the waste paper foams produced with the TEDA catalyst are stiffer compared to those produced without the catalyst.

Table 6: Elastic modulus of waste paper foam produced with and without the TEDA catalyst.

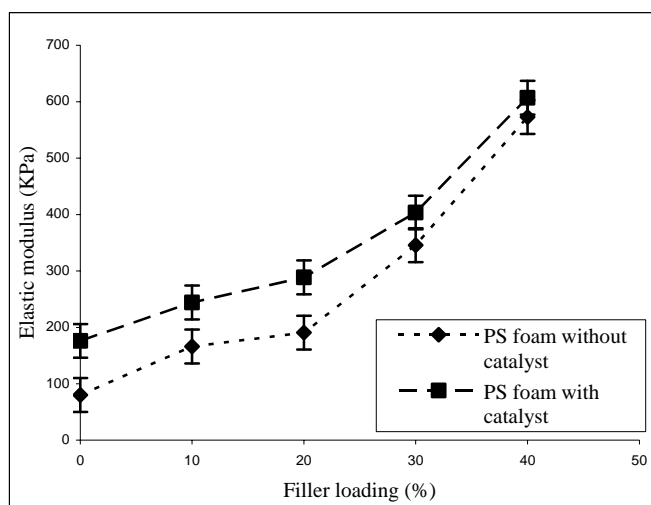| Filler loading (%)	Elastic Modulus (KPa)					
	Without Catalyst			With Catalyst		
	PS foam	OWP foam	ONP foam	PS foam	OWP foam	ONP foam
0	80.2	80.2	80.2	176.05	176.05	176.05
10	166	317.6	401.4	244.11	267	504.55
20	190.7	463.3	610.5	288.58	474.6	708.7
30	345.52	523.3	845.5	403.55	502.82	881.52
40	572.79	794	943.7	607.11	810.35	958.92

Figure 2: The effect of filler content on the elastic modulus of PS foams produced with and without the TEDA catalyst.

The results of hardness of waste paper foam produced with and without the TEDA catalyst are shown in Table 7. Figure 3 presents the hardness of PS foam produced with and without the TEDA catalyst as a function of filler contents. The waste paper foam produced using the catalyst exhibits a higher value of hardness compared to that produced without the catalyst. This indicates that the catalyst may react with the PU to produce a closer packed structure, which could lead to an increase in the hardness of the foam. A higher cross-linking level can lead to the production of smaller cells, and catalysts used in producing PU typically affect the level of cross-linking. Reactive amines containing hydroxyl groups provide higher cross-linking activities, especially in isocyanate activity. It has been reported that hydroxyl groups containing catalysts could react with isocyanate to form a urethane compound, which would be the precursor of isocyanurate formation. Due to the hydrogen bonding between water and the amine catalyst, the water is present in the vicinity of an isocyanate group that is activated by the tertiary amine. The blowing catalyst would have an interaction with the active hydrogen of the urea compound by hydrogen bonding, which would result in the urea compound reacting again with the activated isocyanate to form the biuret compound.[3] Table 7 shows that of the three types of waste paper, the ONP foam with the catalyst has the highest hardness value, followed by the OWP and PS foams.

Table 7: Hardness of waste paper foams produced with and without TEDA catalyst.

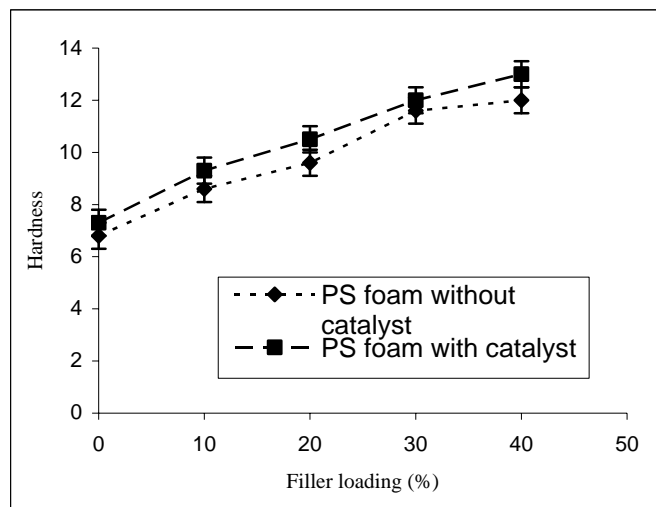| Filler loading (%) | Hardness | | | | | |
| | Without Catalyst | | | With Catalyst | | |
	PS foam	OWP foam	ONP foam	PS foam	OWP foam	ONP foam
0	6.8	6.8	6.8	7.3	7.3	7.3
10	8.6	9.2	9.8	9.3	10	10.56
20	9.6	10.4	11.6	10.5	11.17	12.5
30	11.6	12.2	12.6	12	13	13.7
40	12	13	13.4	13	14	15.3

Figure 3:   The effect of filler content on the hardness of PS foam produced with and without a TEDA catalyst.

4.   CONCLUSION

The effect of TEDA as a catalyst and waste paper filler content on the mechanical properties of waste paper foams has been investigated. The results indicate that increasing the waste paper filler content leads to an increase in compressive strength, elastic modulus and hardness of the foams. In addition, at constant filler content, the waste paper foam composites produced using the TEDA catalyst result in higher values of hardness, compressive strength and elastic modulus compared those produced without the catalyst.

5. REFERENCES

1. Fakas, A. & Flynn, K.G. (1960). The catalytic effects of 1,4-diaza[2.2.2] bicycloöctane for isocyanate reaction. *J. Am. Chem. Soc.*, 82, 642–645.
2. Wong, S.W. & Frisch, K.C. (1986). Catalysis in competing isocyanate reactions. I. Effect of organotin-tertiary amine catalysts on phenyl isocyanate and N-butanol reaction. *J. Polym. Sci. Polym. Chem. Ed.*, 24, 2867–2875.
3. Arai, S., Tamano, Y., Kumoi, S. & Tsutsumi, Y. (1984). Catalytic activities of various tert. amines for the urethane foam reactions. *TOSOH kenkyuhoukoku*, 28(1), 23–34.
4. Okuzono, S., Kisaka, H., Tamano, Y. & Lowe, D.W. (1993). Key aspects of novel catalyst systems in all-water blown integral skin foams, related catalystic activities in the isocyanate reaction. *Proceedings of the Polyurethane World Congress*, Vancouver, 10–13 Oct. 1993.
5. Cooper, W., Pearson, R.W. & Darke, S. (1960). Isocyanate reactions and the structure of polyurethanes. *The industrial chemist,* 36, 121–126.
6. Thiele, L. & Becker, R. (1993). Catalytic mechanisms of polyurethane formation. *Adv. Urethane Sci. Technol.*, 12, 59–85.
7. Maris, R.V., Tamano, Y., Yoshimura, H. & Gay, K.M. (2005). Polyurethane catalysis by tertiary amines. *Journal of Cellular Plastics,* 41(4), 305–322.
8. Blank, W.J., He, Z.A. & Hessell, E.T. (1999). Catalysis of the isocyanate-hydroxyl reaction by non-tin catalysts. *Progress in Organic Coating*, 35, 19–29.
9. He, Z.A., Blank, W.J. & Picci, M.E. (2002). A selective catalyst for two-component waterborne polyurethane coatings. *Journal of Coating Technol.*, 74, 31–36.
10. ASTM D2240-03 (2003). Standard Test Method for Rubber Property – Durometer Hardness. West Conshohocken, PA: ASTM International.