Investigation of Degradation of Structural Adhesives under Influence of Chemicals

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Summary: Structural adhesives are used for joining materials also under conditions, where they through the application will be influenced by many different chemicals. The adhesives can – if not protected from the chemical influence – be degradated of the chemicals. The degradation can because of the different structures of the polymers in the adhesives result in lower strength of the joining area, but can also give higher strength but brittleness.
Information of the structures of the structural adhesives used in the project have been taken from the data sheets from the manufacturers and have been compared with investigation of the structures by FTIR and DSC. In the laboratory the HSP's (Hansen Solubility Parameters) of the adhesives has been determined and compared with the theoretically estimated HSP's. The estimation has mainly been done by Lydersens group contribution method.
The chemical resistance of the adhesives have been foreseen by using HSP's of the adheisves and compared them with the HSP's of the chemicals.
The structural adhesives were most of the epoxy types and of the polyurethane types with different curing systems. The structural adhesives should all have high strength and an opening time of more than 30 minutes. They were in the laboratory cured up after the specifications from the manufacturer and were stored one week after curing before they were influenced by hte chosen chemicals. The chemicals were chosen from their functional groups.
In the laboratory the adhesives were influenced by different chemicals at room temperarture and under elevated temperature and under different periods to develope the degradation curves for the different chemicals and to foresee the degradation time of the adhesives before their properties were not acceptable any more. The structure after influence of the chemicals is studied by FTIR. The results of the investigations have been that it is possible to estimate the degradation by using the HSP's of the adhesives and the chemicals, but to estimate the time before degradation has been so serious that the properties of the adhesives are not acceptable any more, it is necessary to add laboratory investigations to the HSP comparisons of adhesives and chemicals. The comparison of the HSP and of the chemicals by which the adhesives can be in its lifetime has seen to be usefull especially if the chemicals are pesticides.

Keywords: adhesives; degradation

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Introduction

The project called CLEA (Center for lette og elegante konstruktioner i aluminium samlet ved limning) has the main topic to construct the boom of a sprayer for plant protection in aluminium and to assemble the boom using adhesives. The spray boom has a length of 18 meter. Equipments for spraying fertilizers and pesticides on the fields are added under the boom. In thc project Aalborg University Esbjerg has the main topic to find the adhesive regarding chemical resistance against the pesticides and fertilizers and adhesion to the Aluminium surface. The strength of the adhesive is important, too, why only structural adhesives has been regarded. 3M is a partner in the project, why it is structural adhesives manufactured by 3M that had been investigated. In this part only the chemical resistant of the adhesives will be treated. The strength of the adhesives and the adhesion to the Aluminium surfaces will not be treated here. The investigations of the chemical resistance of the adhesives were made by comparing the Hansen Solubility Parametres (HSP) of pesticides and fertilizers with the HSP's of the cured adhesives. The adhesives were cured at room temperature and at 60°C to investigate if the curing temperature had any influence of the chemical stability of the adhesives in contact with the chosen chemicals. A group of pesticides and NPK-fertilizer were decided to be used as examples because there are too many pesticides to take them all. The HSP's were used as a screening of the chemical resistans because it is too time consuming and therefore too expensive to test all adhesives against all the possible chemicals. The structure of the adhesives is investigated by FT-IR. The glass transition temperature of the adhesives is measuared by DSC. The HSP for the adhesives are determined experimentally by using a group of solvents with wellknown solubility parameters. The HSP for the pesticides are calculated by using the Lydersens Group Contribution method. In the project it was decided to use the adhesives DP125, DP190, DP410, DP460, DP610 and DP810. All of them are structural adhesives from 3M with theorethical high enough strength for the spray boom. The adhesives have been selected by 3M because of the mechanical properties set up as requirements for the adhesive. The adhesives DP 460 and DP 610 has been examined special.

Requirements

The requirements for the adhesive for the spray boom were set up from the mechanical, the thermal and the chemical load on the boom.

The requirements were

- good mechanical strength, because of the high load of weigth on the boom,
- flexibility, because of the movements in the boom, when the tractor with the spray boom is driving over fields
- mechanical properties and flexibility in the temperature area –10°C and up to 50°C because of the different temperatures all over the world
- chemical resistant against pesticides used for plant protection, fertilizers, water, cleaning agents (mainly acids and bases and surfactants)
- UV-resistance
- 20.000 working hours under influence of chemicals and UV radiation
- adhesion to Aluminium
- processable, because the adhesive shall be able to flow through an 18 meter long channel in the spray boom
- opening time 30 - 60 minutes because of the flow way after injection
- curing at room temperature, because of the size of the boom

If not all requirements could be fulfilled, it would be necessary to decide which were the most important. The primary requirements were decided to be the mechanical properties (strength and flexibility, no brittleness), the temperature resistance and the processability of the adhesive. If the adhesive can be resistance against chemicals and UV radiation it would be good, but if it was not possible to find an adhesive with all the properties, the adhesive could be protected.

Chemicals Used in the Investigation

The inorganic fertilizers were regarded as NPK-fertilizer. The pesticides were from various different types, giving enormous problems; therefore it was necessary to decide which pesticides we should use in the project. Together with the producer of the spray boom it was decided to use 24 rather common used pesticides. They are listed in table 3.

Some of the pesticides are liquids and some are solids at room temperature. They are dissolved, emulgated or made as a supsension in different solvents. They are mixed or used as one-component system. In the investigations the pesticides have been regarded as single components all of them.

The cleaning agents are mainly acidly or basicly liquids. For illustrating the effects of the cleaning agents we have used NaOH and HCl. For illustrating the effects of a group of pesticides we have chosen chemicals with functional groups as a widely part of the pesticides.

Theory

A through experimental investigation of the chemical resistance to all the possible chemicals at all the adhesives is comprehensive, time comsuming and expensive. For decrease the amount laboratory experiments it was decided to use the Hansen Solubility Parameters, HSP, for estimation of the chemical resistance of the adhesive and the chemicals.
The HSP's were calculated for pesticides with the group contribution method to predict the chemical influence and resistance of one of the adhesives.

The total solubility parameter,δ, is defined as

$$\delta = (E/V)^2,$$

where

E is the energy of evaporation
V is the molar volumen.

Using the HSP the solubility parameter is splitted up in

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2,$$

where

δ_d is the contribution from the dispersion bonds

δ_p is the contribution from the polar bonds

δ_h is the contribution from hydrogen bonds.

(1)

For the HSP's a polymer will be a sphere with an interaction radius, Ro. The solvents – and here all the fertilizers and the pesticides – the HSP's will be regarded as just a point, though well-known they can have an action radius as well. The modified difference between a solvent and a polymer is Ra, where Ra is the distance between two materials based on their respective partial solubility parameters. Ra can be expressed as (1)

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2.$$

The ratio between Ra and Ro is called the Relative Energy Difference, RED, and is used for predicting whether a solvent can dissolve (or swell) a polymer or not.

$$RED = Ra/Ro.$$

A RED-number of 0 indicates affinity between the two materials. A RED-number less than 1 indicates high affinity between the two materials. A RED-number equal to or close to 1 is a boundary condition.RED-numbers higher than 1 indicates progressively lower affinities.

In this case a RED-number less than one for the pesticide/adhesive couple will be regarded as possibility for interaction between the adhesive and the pesticide.

For a material or a solvent the HSP's can be estimated using the group contribution method. The group contribution method is based on the assumption that the contribution from different functional groups to the thermodynaic properties are additive. This is the case for the one-dimensional solubility parameters. Using the three dimensional Hansen solubility parameters, the rules of simple addition is not adequate. Under the method of Hoftyzer and van Krevelen, which is used in this work, the estimating of the solubility parameters is made out from the two different tables. The values for the three partiel contributions was found in tables compiled by Hoftyzer and van Krevelen whereas the group molar volumes were found in a table compiled by Fedors. (2). The later may give less accurate estimates than other tables containing group molar volumes, but used here since it is more comprehensive. None of the used tables are adequate, why certain assumptions are made.

The Adhesives Used in the Investigations

The adhesives were all structural adhesive, which means that they have a high mechanical strength.

They have mainly been chosen out from their mechanical properties and because they have good adhesion to aluminium. The aluminium used for the spray boom was the aluminum alloy 6063, which contain Mg and Si as alloy elements. The spray boom should be extruded in profiles and the alloy 6063 has good strength, is good for extrusion and has the chemical resistance for outdoors use.

The adhesives have the following base resins

- DP125 epoxy/amine resin
- DP190 epoxy/amine resin
- DP410 toughened epoxy/modified amines
- DP460 epoxy/amine resin
- DP610 polyol/isocyante resin
- DP810 arylic

All the adhesives can cure up at room temperature, but the curing time decreases and the strength of the adhesive increases at elevated temperature. The curing times for all the adhesives are 24 hiurs at room temperature or 2 hours at 71°C.

In the laboratory we cured all the adhesives 24 hours at room temperature and 4 hours at 60°C.

After curing the maximum strength of the adhesives are obtained after 7 days and the maximum chemical resistance are obtained after 7 days. The adhesives were stored 7 days at room temperature before influenced of chemicals.

The adhesive DP460 was used for making estimations for the chemcial influence of the pesticides from the method comparing the HSP's for the adhesive and the pesticides.

Experiments

In the laboratory the HSP's of DP460 cured at room temperature and cured at 60°C was measured using 31 chemicals with wellknown HSP. Table 1 shows the list of chemicals with their partial solubility paramaters.

For determining the solubility parameters of the adhesive DP460 a small amount of the adhesive is placed on cover glasses. The adhesives are cured up as mentioned above. 31 glasses with adhesive were prepared. The adhesive is a thermoset and it is expected that it will take some days before there will be any interaction between the adhesive and the solvents.

Table 1. Solubility parameters for the used solvents (3). The values in the brackets are taken from (1) and they are included because they differ from the values in (3). The other values are the same in the two references.

NO	Name	HSP (MPA^{½})		
		δD	δP	δH
1	Acetone	15,5	10,4	7,0
2	1,1 Dichlorethylen	17,0(16,4)	6,8(5,2)	4,5(2,4
3	1,2 propandiol (propylenglycol)	16,8	9,4	23,3
4	1,4 Dioxan	19,0	1,8	7,4
5	1-Butanol	16,0	5,7	15,8
6	4-Methyl-2-pentanon	15,3	6,1	4,1
7	Acetophenon	19,6	8,6	3,7
8	Chlorbenzen	19,0	4,3	2,0
9	Chloroform	17,8	3,1	5,7
10	Cyklohexanol	17,4	4,1	13,5
11	Cyklohexanon	17,8	6,3	5,1
12	Diethylether	14,5	2,9	5,1
13	Diemethylsulfoxid	18,4	16,4	10,2
14	Ethanolamin	17,2(17,0)	15,5	21,3(21,2)
15	Ethylacetat	15,8	5,3	7,2
16	Ethylenglycol	17,0	11,0	26,0
17	Ethylenglycolmonobutylether	16,0	5,1	12,3
18	Ethylenglycolmonomethylether	16,2	9,2	16,4
19	Formamid	17,2	26,2	19,0
20	γ-butyrolactone	19,0	16,6	7,4
21	Hexan	14,9	0,0	0,0
22	Isophoron	16,6	8,2	7,4
23	Methanol	15,1	12,3	22,3
24	Methylenclorid	18,2	6,3	6,1
25	Methylethylketon	16,0	9,0	5,1
26	Morpholin	18,8	4,9	9,2
27	N,N Dimethylformamid	17,4	13,7	11,3
28	Tetrahydrofuran	16,8	5,7	8,0
29	Toluen	18,0	1,4	2,0
30	Trichlorethylen	18,0	3,1	5,3
31	Nitrobenzene	20,0	8,6	4,1
32	n-Butylacetate	15,8	3,7	6,3

Table 2. The used solvents and their effect on the adhesive.

NO	Name	Swelled		No interaction		Interaction	
		20 ^{0}C	60 ^{0}C	20 ^{0}C	60 ^{0}C	20 ^{0}C	60 ^{0}C
1	Acetone	X					
2	1,1 Dichlorethylen				X	X	
3	1,2 propandiol (propylenglycol)			X	X		
4	1,4 Dioxan	X					X
5	1-Butanol			X	X		
6	4-Methyl-2-pentanon				X	X	
7	Acetophenon				X	X	
8	Chlorbenzen	X					X
9	Chloroform	X	X				
10	Cyklohexanol			X	X		
11	Cyklohexanon					X	X
12	Diethylether			X	X		
13	Diemethylsulfoxid					X	X
14	Ethanolamin			X	X		
15	Ethylacetat					X	X
16	Ethylenglycol			X	X		
17	Ethylenglycolmonobutylether			X	X		
18	Ethylenglycolmonomethylether					X	X
19	Formamid			X	X		
20	Gamma-Butyrolacton				X	X	
21	Hexan			X	X		
22	Isophoron				X	X	
23	Methanol					X	X
24	Methylenclorid	X	X				
25	Methylethylketon	X					X
26	Morpholin	X			X		
27	N,N Dimethylformamid	X					X
28	Tetrahydrofuran	X	X				
29	Toluen	X					X
30	Trichlorethylen	X	X				

For measuring the HSP's solvents were filled in small glass bottles and the cover glass/adhesives are submerged into the glass bottles. The bottles are closed with lids. The 62 bottles were kept at room temperature for three days. After three days the samples were evaluated and categorized in swelled, interaction or no interaction. Swelled covers samples which after three days in the solvents easily falls apart. Interaction covers samples with changes in the surface. The evaluation of the samples can be seen in Table 2.

In the laboratory all the adhesives were put on a cover glass and cured up as mentioned above. After 7 days chemicals were put on the adhesives. The adhesives with the chemicals on were stored at room temperature, 40°C and 60°C in 1 day, 7 days and 28 days.

The chemicals were 0,1 M HCl, 0,1M NaOH, butanal, iospropylalcohol, NPK-fertilizer dissolved in water, tetrachloroethylen and a reference with no chemical influence to control if an eventually change in the adhesives should be the temperature and time influence more than the chemical influence.

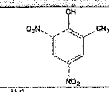
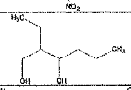
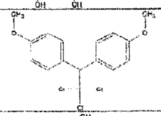
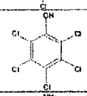
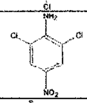
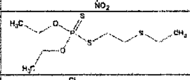
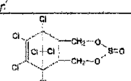
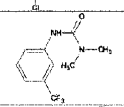
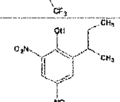
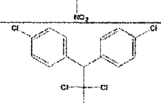
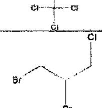
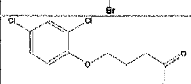
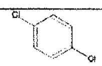
The test was made in a way that statistical analysis of the result was possible.

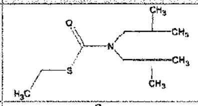
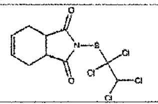
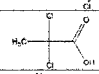
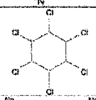
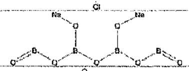
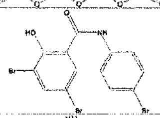
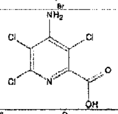
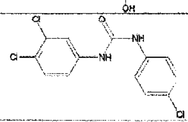
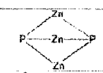
The adhesive DP460 and DP610 were measured after curing at room temperature and 60°C at FTIR and at DSC to see if they gave the same result for curing at room temperature and at 60°C or differed in results.

Calculations of the HSP Using the Group Contribution Method

The HSP for the pesticides has been calculated and not measured experimentally. For the calculations the two tables compiled by Fedors and by Hoftyzer and van Krevelen respectively has been used. Group molar volumes were found in the table of Fedors while the values for the single forces, the dispersion forces, the polar forces and the hydrogen forces, were found in the tables of Hoftyzer and van Krevelen. Using the values the HSP for the 24 pesticides has been calculated as seen in Table 3.

Table 3. The name, structure, formula and type of the 24 pesticides investigated. The HSP and the RED are calculated for the pesticides.

Name	Structure	Formula	Type	HSP			RED	
				δ_D	δ_P	δ_H	20°C	60°C
Nitrophenol		$C_7H_6N_2O_5$	acaricide fungicide herbicide Insecticide	23.8	13.1	13.7	1.4	3.8
Ethylhexanediol		$C_8H_{18}O_2$	Insecticide	16.7	4.7	16.4	1.4	2.4
Methoxychlor		$C_{16}H_{15}Cl_3O_2$	Insecticide	15.2	4.6	2.7	0.9	1.5
Pentachloro-phenol		C_6Cl_5OH	herbicide	35.1	12.5	14.4	3.4	8.1
Dichloran		$C_6H_4Cl_2N_2O_2$	fungicide	26.0	11.7	9.7	1.5	4.1
Disulfoton		$C_8H_{19}O_2PS_3$	Insecticide	18.6	5.4	5.2	0.4	0.6
Endosulfan		$C_9H_6Cl_6O_3S$	pesticide	26.6	8.3	7.2	1.6	4.0
Fluometuron		$C_{10}H_{11}F_3N_2O$	herbicide	16.9	7.8	8.0	0.6	1.3
Dinoseb		$C_{10}H_{12}N_2O_5$	herbicide	21.5	9.4	11.6	0.9	2.4
DDT		$C_{14}H_9Cl_5$	insecticide	22.4	5.8	3.1	0.8	2.2
Dibromochloro-propan		$C_3H_5Br_2Cl$	fumigant	18,8	6,8	2,6	0,3	1,2
Butoxone		$C_{10}H_{10}Cl_2O_3$	herbicide	19.0	6.0	9.2	0.6	1.1
Dichloro-benzen(p)		$C_6H_4Cl_2$	fumigant	21.6	7.8	2.8	0.6	2.1

Name	Structure	Formula	Type	HSP			RED	
				δD	δP	δH	20°C	60°C
Butylate		$C_{11}H_{23}ONS$	herbicide	17.5	5.4	5.7	0.5	0.6
Captafol		$C_{10}H_9Cl_4NO_2S$	fungicide	36.6	14.6	9.3	3.6	8.7
Dalapon		$C_3H_4Cl_2O_2$	herbicide	23.8	11.8	12.0	1.3	3.5
Amitrole		$C_2H_4N_4$	herbicide	18.0	27.7	22.7	2.6	6.6
Lindane		$C_6H_6Cl_6$	insecticide	27.0	8.4	3.9	1.6	4.2
Borax		$Na_2B_4O_7$	fungicide	-----	-----	-----	-----	-----
Polybrominate salicylanilides		$C_{13}H_8Br_3NO_2$	bakteriostat	27.5	7.6	12.2	1.9	4.6
Picloram		$C_6H_3Cl_3N_2O_2$	herbicide	34.1	13.1	15.6	3.3	7.8
TCC		$C_{13}H_9Cl_3N_2O$	fungicide	25.3	7.2	7.3	1.3	3.4
Zinc phosphide		Zn_3P_2	rodenticide	-----	-----	-----	-----	-----
Sodium arsenate		Na_2HAsO_4	insecticide herbicide	-----	-----	-----	-----	-----

It gave some problems to divide the pesticide molecules into functinal groups. Besides that the tables used lack several values needed for the calculations. For the calculations some assumptions has been made. These assumotions together with the dividing of the molecules cause certain uncertainties, and reservations must be made to some of teh results. The group contribution method disregards the effect of neighboring groups.

Results and Discussion

The HSP's for DP460 was measured for theadhesive sured at room temperature and cured at 60°C.

The HSP's for DP460 cured at room temperature were found to be

$\delta_d = 19.0$ $\delta_p = 9.0$ $\delta_h = 4,6$, with the interaction radius of the sphere Ro = 9.9.

For DP460 cured at 60°C the result was

$\delta_d = 18.0$ $\delta_p = 2.9$ $\delta_h = 6.2$, with the interaction radius of the sphere Ro = 4.5.

From the results it can be seen that the center of the sphere has moved a little but more important is it that the interaction radius has decreased for curing at high temperature. The chemical resistance will probably be increased if the adhesive is cured up at elevated temperature.

The FTIR showed that both DP460 and DP610 have the same specter if they are cured at low or high temperature.

The DSC-scan showed for both of the adhesives that the glass transistion temperature increased by increasing the curing temperature.

Both results were expected.

The measuring of the chemical resistance for all the adhesives was given marks from 1 to 5 after the change in the adhesive. We marked with 1 as the best (no changes) and 5 as worst case. We marked the changes after change in colors, change in hardness and change in structure. We compared with a sample stored the same time at room temperature.

The results of the chemical influence were that four epoxy based adhesives had better chemical resistance than the acrylic adhesive and than the polyurethan adhesive. Wre found that the time and the temperature have an influence on the destruction of the adhesives under influence of chemicals.

The different chemicals influenced the adhesives different.

We found that the organic substances had more influence than the NPK-fertilizer. 0,1M HCl and 0,1M NaOH influenced especially the DP610.

We found that none of the adhesives were totally resistance for the chemicals. Out from that DP460 was chosen as the adhesive we would use for the spray boom. DP460 hold most of the other requirements good and it was decided that the adhesive should be protected against chemical influence as must as possible.

The RED-number for the pesticides and DP460 has been calculated. The result can be seen in table 3.

Out from the RED-numbers it can be seen that risk for influence of the pesticides on DP460 are higher if the adhesive is cured up at room temperature.

In Table 4 the possible chemical influence out form the calculated RED-number are listed.

Table 4. Categorizing of pesticides due to their RED-numbers for curing temperatures at room temperature and at 60°C.

Curing temperature RT		
Hazardeous	***Possible hasardeous***	***Not hasardeous***
Methoxychlor	Nitrophenol	Pentachlorophenol
Disulfoton	Ethylhexanediol	Captafol
Fluometuron	Dichloran	Amitrole
Dinoseb	Endosulfan	Picloram
DDT	Dalapon	
Dibromochloropropan	Lindane	
Dichlorobenzen(p)	Polybrominatesalicylanilides	
Butoxone	TCC	

Table 4 continued.

Curing temperatur 60^0C		
Hazardeous	***Possible hasardeous***	***Not hasardeous***
Disulfoton	Methoxychlor	Nitrophenol
Butylate	Fluometuron	Ethylhexanediol
	Dibromochloropropan	Pentachlorophenol
	Butoxone	Dichloran
		Endosulfan
		Dinoseb
		DDT
		Dichlorobenzen(p)
		Captafol
		Dalapon
		Amitrole
		Lindane
		Polybrominatesalicylanilides
		Picloram
		TCC

Form the table it can be seen that curing at high temperature give significant better chemical resistance than curing at room temperature. This was expected due to the smaller interaction radius of the spheres for the DP460 at the two temperatures.

In the calculations it has not been looked at at all if the pesticides are liquids or solids and possible solvents for the pesticides have not been regarded either.

Conclusion

From the experiments and the calculations it can be seen that it is possible to estimate the chemical resistance of adhesives. The chemical resistance can be estimated using the Hansen solubility parameters, but have long time it will run before the degration of the adhesive is so far that it cannot be used anymore cannot be estimated by this method. For estimating the time for degradation laboratory experiments must be done additionally.

From measuring the chemical resistance it was found than none of the adhesives had very good chemical resistance over a long period. DP460 was decided as the best adhesive by comparing with all the requirements. DP460 will have better chemical resistance if the production can be set up in a way that the curing of the adhesive can take place at elevated temperature.

The estimation by using the Hansen solubility parameters are less time consuming than experiments and can be used as a good screening for the chemical resistance.

1) Hansen, C.M., *Hansen Solubility Parameters: A user's Handbook*, CRC Press LLC, 2000
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3) Nicholas,P., *Handbook of Polymer Science and Technology*, M.Dekker,cop.1989