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Optimization of Process Parameters and Adhesive Properties of Liquid Epoxidized Natural Rubber/Epoxy Blends

Zuraidah Zainudin, Gaura Chandrika Arumugam, Siti Hajjar Che Man*, Norfhairna Baharulrazi, Zurina Mohamad

Department of Chemical Engineering, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
sitihajjar@utm.my

The use of adhesives marks a new epoch in the structure-joining technology as using polymeric material is more sustainable, lower possible curing temperature, fine pitch capability and lightweight as compared to tin-lead soldering. In this study, the optimization of process parameters such as curing time and Liquid epoxidized natural rubber (LENR) loading was carried out using central composite design (CCD) in response to surface methodology (RSM) to determine the optimum condition for achieving maximum adhesive properties (shear strength and peel strength) of epoxy/liquid epoxidized natural rubber (LENR) blend. Analysis of variance (ANOVA) analysis shows that the coefficient of determination for both shear and peel strength models were 0.9838 and 0.9909 indicating a high correlation between the actual values and predicted values. The optimum conditions for a maximum predicted shear strength value of 8.37 MPa was 20.65 parts per hundred rubber (phr) liquid rubber (LR) loading for 6.94 curing days and for a maximum predicted peel strength value of 500 J/m was 18.44 phr for 3.75 curing days. This study reports under optimized conditions, it showed the potential of LENR as one of the most effective ways to improve the adhesive properties of epoxy resin.

1. Introduction

Epoxy resin is commonly used for adhesive applications due to many advantageous properties such as excellent resistance to moisture, solvents and chemical attacks, good thermal resistance, low shrinkage, excellent adhesive strength and mechanical strength (Pham et al., 2017). The excellent properties of the epoxy resin are based on the hydroxyl, epoxy groups, bisphenol-A and ether linkages. The hydroxyl and epoxy groups give the adhesive properties or reactive site to curing agents while bisphenol A provides the rigidity, toughness and maintain the properties of epoxy resin at elevated temperature. The ether linkage gives the chemical resistance to the epoxy resin. The conventional epoxy-based adhesives have very limited application in the industry due to after cured process with the hardener, it becomes brittle and exhibits poor resistance to crack initiation and propagation (Saba et al., 2016). An improvement of the adhesive strengths can be achieved by using flexibilizers or toughening agents (Xu et al., 2019). One of the most promising ways to produce high performance adhesives with optimum mechanical, thermal, and chemical properties is the addition of suitable reactive rubbers. The formation of two-phase morphology during the curing process by controlled precipitation of rubbery particles from the initially compatible thermoset-elastomer mixture is widely accepted as the cause of the improved impact and adhesive strength (Kinloch et al., 1983).

In earlier investigations, the problems of lack of compatibilization do exist in rubber-epoxy systems which highlight that high molecular weight of rubber such as natural rubber (NR) and epoxidized natural rubber (ENR) decreased the adhesive properties of epoxy resin itself due to their lack of compatibility between rubber and epoxy resin. For example, Hong et al. (2005) investigated the adhesive properties of the resulting blend decreased beyond the addition of 5 phr of ENR which is due to the limited compatibility of the high molecular weight of ENR with the epoxy system matrix. The presence of polar group such as epoxide group in LENR can enhance the polarity and reactivity of the liquid natural rubber and increase the compatibility of LENR with the epoxy matrix (Mohammad et al., 2018). LENR has been used as toughening agent for epoxy composite to

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improve mechanical properties such as tensile strength and impact strength (Mohammad et al., 2018). The studies of LENR as toughening agent for epoxy adhesives has not yet to be conducted.
For common adhesive application, cold-curing resins can be utilised where epoxy systems are cured at room temperature to achieve a suitable degree of cure with acceptable mechanical and adhesive properties. Aliphatic amine can be utilised as curing agents for cold curing process since they are able to form covalent bond between epoxide group in epoxy resin at room temperature. It is necessary to determine the curing time where epoxy can acquire maximum degree of crosslinking at room temperature where higher degree of crosslinking indicate better mechanical and adhesive properties (Lettieri and Frigione, 2012). In this study, cold curing process is applied to epoxy systems where epoxy is cured with curing agent such as aliphatic amine at room temperature. Response surface methodology (RSM) is a multivariable technique that simultaneously optimizes the process parameters to get best response within the experimental region under study (Favre et al., 2020). RSM can reduce required time and effort to differentiate the interaction effects between those individual factors compared to conventional methods which may investigate one independent factor with other factors fixed at one time (Birgen et al., 2018). The main objective of the work was to use RSM based on CCD to obtain optimum preparation conditions for preparation of LENR/epoxy adhesives and provides a solid background for future fabrication of LENR/epoxy adhesives. Regression models for each model were generated and verified. Two numerical variables (curing time and loadings of LENR) are the independent variables while shear strength and peel strength of LENR/epoxy adhesives are the dependent variables.

2. Methodology

2.1 Design of experiment

In this design experiment, the shear strength and peel strength were taken as the end results and were affected by a variety potential variable (curing time and LENR loading). Other controlled variable such as curing temperature are maintained at room temperature throughout the designing experiment. The Design Expert software version 12 was used to generate experiment value from three-level-two-factor central composite rotatable design (CCRD) procedure and analysed by Response Surface Methodology (RSM) and also for determined the effect of independent variables on response and optimize the shear strength and peel strength (Zhang et al., 2021). A 4 factorial points, 4 axial points and 5 center points was employed to generate the experiment data for RSM models. The range values of the process parameters (independent variables) namely the curing time and loadings of LENR in epoxy matrix are 5 - 25 phr and 2 - 6 d and is set based on common range used by past literatures. The coded values were listed in Table 1.

Table 1: Coded and actual values of process parameters

Variable	Levels		
	-1	0	+1
LENR: Epoxy weight ratio, (phr) (X1)	5	15	25
Curing time, (d) (X2)	2	4	6

-1 is low value, +1 is high value, 0 is central value, -α is low star value, +α is high star value

2.2 Data collection

In normal practices, the response data for the DOE table has to be obtained from experimental works. Due to inability to perform the needed experimental works, matching data from literatures closest to current case study is used as a substitute. Due to limited sources on LENR/epoxy adhesives from past literatures, literatures on liquid synthetic rubber toughened epoxy adhesives has been used for the response data. The liquid epoxidized natural rubber and epoxy-terminated liquid synthetic rubber derived from carboxyl-terminated butadiene acrylonitrile liquid rubber (CTBN) are assumed to have almost similar curing mechanism due to its reactive group being similar (epoxy-terminated rubbers). The response data used for the DOE table in this research was extracted from past literatures that experimented on epoxy adhesives toughened with liquid rubber namely CTBN (Achary et al., 1990), carboxyl-terminated poly(2-ethyl hexyl acylate) (CTPEHA) (Ratna and Banthia, 2000), carboxyl-randomized poly(2-ethyl hexyl acrylate) (CRPEHA) (Kar and Banthia, 2003), and epoxidized soybean rubber (ESR) (Ratna and Banthia, 2000). In order to reduce the random error in the group of data collected, the process parameter range and DOE matrix was modified until it matches the available data. Most of the data collected was limited to epoxidized carboxyl-terminated rubber toughened epoxy adhesives, adhesives with post curing between the range of 70 - 80 °C and machine crosshead speed of 10 - 20 mm/min in Lap shear strength test and 10 - 200 mm/min for T-Peel test (Ratna and Banthia, 2000).

3. Results and discussion

3.1 Optimization study of LENR/epoxy blend

Central composite design and response surface methodology was used to analyse the interactions between the variables and the impact on the responses investigated namely shear and peel strength. Table 2 and 3 are the input matrix created via data collection from past literatures.

Table 2: Design matrix of Central Composite Design shear strength

Number of runs	Combination of process parameter				Shear strength (MPa)	Source of data
	Coded values		Actual values			
	X1	X2	X1	X2		
1 Design centre point	0	0	15	4	7.74	(Achary et al., 1990)
2	0	0	15	4	7.74	(Achary et al., 1990)
3	0	0	15	4	7.74	(Achary et al., 1990)
4	0	0	15	4	7,74	(Achary et al., 1990)
5	0	0	15	4	7.74	(Achary et al., 1990)
6 Axial or star points	-1.414	0	0.86	4	4.83*	(Ratna and Banthia, 2000a)
7	+1.414	0	29.14	4	6.62*	(Ratna and Banthia, 2000a)
8	0	-1.414	15	1.17	7.06	(Achary et al., 1990)
9	0	+1.414	15	6.83	8.35	(Achary et al., 1990)
10 Factorial points	-1	-1	5	2	6.50	(Ratna and Banthia, 2000a
11	+1	-1	25	2	6.75	(Ratna and Banthia, 2000a)
12	-1	+1	5	6	5.88	(Ratna and Banthia, 2000b)
13	+1	+1	25	6	8.00	(Ratna and Banthia, 2000b)

X1 is for LR loading in phr, X2 is cure time in d, Values based on assumption (*)

Table 3: Design matrix of Central Composite Design for peel strength

Number of runs	Combination of process parameter				Peel strength (J/m)	Source of data
	Coded values		Actual values			
	X_1	X_2	X_1	X_2		
1 Design centre point	0	0	15	4	490*	(Ratna and Banthia, 2000a)
2	0	0	15	4	490*	(Ratna and Banthia, 2000a)
3	0	0	15	4	490*	(Ratna and Banthia, 2000a)
4	0	0	15	4	490*	(Ratna and Banthia, 2000a)
5	0	0	15	4	490*	(Ratna and Banthia, 2000a)
6 Axial or star points	-1.414	0	0.86	4	242.85*	(Ratna and Banthia, 2000a)
7	+1.414	0	29.14	4	414.29*	(Ratna and Banthia, 2000a)
8	0	-1.414	15	1.17	450*	(Nakao and Yamanaka 1992)
9	0	+1.414	15	6.83	408.94*	(Achary et al., 1990)
10 Factorial points	-1	-1	5	2	364.29	(Ratna and Banthia, 2000a)
11	+1	-1	25	2	435.71	(Ratna and Banthia ,2000a)
12	-1	+1	5	6	320.01	(Ratna and Banthia, 2000b)
13	+1	+1	25	6	446.67	(Ratna and Banthia, 2000b)

X_1 is for LR loading in phr, X_2 is cure time in d, Values based on assumption (*)

The results of Table 2 and 3 was fitted into second order polynomial. Eq(1) and (2) below is for shear strength model and peel strength model. Note that model for shear strength has undergone model improvement due to the presences of an insignificant term. All terms in peel strength model is significant.

$$Shear\ strength, S\ (MPa): Si\ = +5.38074 - 0.1972A + 0.2649B + 0.0234AB - 0.010B^2 \quad (1)$$

$$Peel\ strength, P\ (J/m): P = +188.7739 + 38.1358A + 26.0104B + 0.6905AB - 6.7756A^2 - 0.7755B^2 \quad (2)$$

where A is for cure time and B is for liquid rubber (LR) loading in epoxy matrix.

3.2 ANOVA analysis

An ANOVA table summarises all the needed information to test the significance of both the main model and individual coefficient/terms in the regression model. Table 4 and Table 5 shows the ANOVA table for shear

strength and peel strength. Both shear and peel strength models are significant due to “The Prob.>F” in both tables is less than 0.05 (Idris et al., 2019). This also indicates that the terms in the regression model has impact on the responses investigated. In both cases, the lack of fit test is also insignificant which is good because it shows that the model has good fitness.

Table 4: ANOVA for shear strength

Source	Sum of squares	Degree of freedom	Mean square	F	Prob.> F	Remarks
Model	11.57	4	2.89	121.40	<0.0001	Significant
A-cure time (d)	0.7530	1	0.7530	31.59	0.0005	Significant
B- LR loading (phr)	3.00	1	3.00	125.99	<0.0001	Significant
AB	0.8742	1	0.8742	36.68	0.0003	Significant
B2	6.94	1	6.94	291.33	< 0.0001	Significant
Residual	0.1907	8	0.0238			
Lack of fit	0.1907	4	0.0477			Not significant
Pure error	0.0000	4	0.0000			Not significant
R^2	0.9838					
Adj.R^2	0.9757					

Table 5: ANOVA for peel strength

Source	Sum of squares	Degree of freedom	Mean square	F	Prob.> F	Remarks
Model	69946.80	5	13989.36	152.36	<0.0001	Significant
A-cure time (d)	1043.96	1	1043.96	11.37	0.0119	Significant
B- LR loading (phr)	24258.64	1	24258.64	264.21	<0.0001	Significant
AB	762.86	1	762.86	8.31	0.0236	Significant
A2	5109.88	1	5109.88	55.65	0.0001	Significant
B2	41839.24	1	41839.24	455.68	<0.0001	Significant
Residual	642.72	7	91.82			
Lack of fit	642.67	3	214.24			Not significant
Pure error	0.00	4	0.00			Not significant
R^2	0.9909					

Based on the F values in Table 4, it shows that the effect of LR loading in epoxy matrix is greater compared to cure time on the shear strength. Cure time has less impact on the shear strength as its quadratic effect is insignificant and can be removed. For Table 5 effect of LR loading in epoxy matrix is lesser than cure time’s effect on the peel strength. In the mathematical model of peel strength, all the individual term is significant. This result is expected as rubber ratio to epoxy indeed has tremendous impact on its adhesive properties. This is because incorporation of rubber into the epoxy matrix creates a toughening effect which in turn increases the adhesive strength (Kausar, 2020). The rubber and epoxy particles have different particle sizes and structure. When rubber is added into the matrix, a bimodal distribution is formed-locked system that creates the toughening effect. The phase separation only occurs when rubber content is less than or at optimum levels. Above optimum levels, the bimodal separation becomes continuous and there is no visible lock system formed, and led to flexibilization causing the blend to lose rigidity and become brittle (Mohammad et al., 2018). Although cure time has relatively lesser impact on the shear and peel strength of the blend, but its effects are considered significant as well. Cure time determines the percentage of completion of cross-linking in a curing process (Garete et al., 2019). Increase in cure time drives the blend towards completion of cross-linking and led to increasing the toughening effect on the epoxy.

The R^2 values of both peel and shear strength is close to 1 namely 0.9909 and 0.9838. The adjusted R^2 values are 0.9844 and 0.9757. The adjusted R^2 values shows the actual reliability of the mathematical model. This is because R^2 usually increases when more individual terms are added to the mathematical model regardless of whether the addition improved the model fitness or not. For adjusted R^2 the value only increases when addition of removal of individual term improves model fitness. In this case, both the shear and peel strength models met all requirements. Based on the reasons above, both models are feasible.

3.3 Response surface plot analysis

Figure 1a and 1b demonstrates the interactions between cure time and LR loading in 3D-response surface plots of actual values. Based on the Figure 1a and 1b shown it can be seen that LR loading trend has a more visible curve and cure time trend is a linear line. From Figure 1a, it is also evident that increase in cure time causes

increase in shear strength. The increment of shear strength with increasing cure time is possible as increase in cure time will drive towards completion of cross linking between epoxide group in LENR and epoxy and amine groups in curing agent which in turn ensures maximum toughening effects (Savvilotidou et al., 2017). Similar finding was reported by Corcione et al. (2014) where the study observed higher degree crosslinking with increasing curing time. Based on the graph in Figure 1b, it shows increase in the peel strength with increasing cure time till a maximum and then slight drop in the peel strength value. The observation might due to the presence of greater random in collecting data for the peel strength which was used to develop the mathematical model since data is obtained through matching data from literatures closest to current case study and also limited literatures related to liquid rubber/epoxy adhesives. The increasing trend in LR loading causes increase in shear strength and peel strength till a certain optimum value and subsequently drops, forming the curve line. For peel strength, the cure time graph has a slight curve. Optimization of process parameters was done using the numerical optimization method. The condition constraints employed for the optimization are as shown in Table 6 below.

Table 6: Optimization constraints

Aspects	Goals	Minimum	Maximum	Importance rating
Cure time (d)	In range	2	6	3
LR loading (phr)	In range	5	25	4
Shear strength (MPa)	maximize	8.3	8.4	5
Peel strength (J/m)	maximize	490	501	5

Based on the response plots in Figure 1a, the maximum shear strength is obtained for blend of 20.65 phr for a cure time of approximately seven days (6.94 d). The shear strength value reported at those conditions are 8.37 MPa. Meanwhile based on Figure 1b, maximum peel strength is obtained for blend with 18.44 phr for a cure time of approximately four days (3.75 d) which is 500.2 J/m.

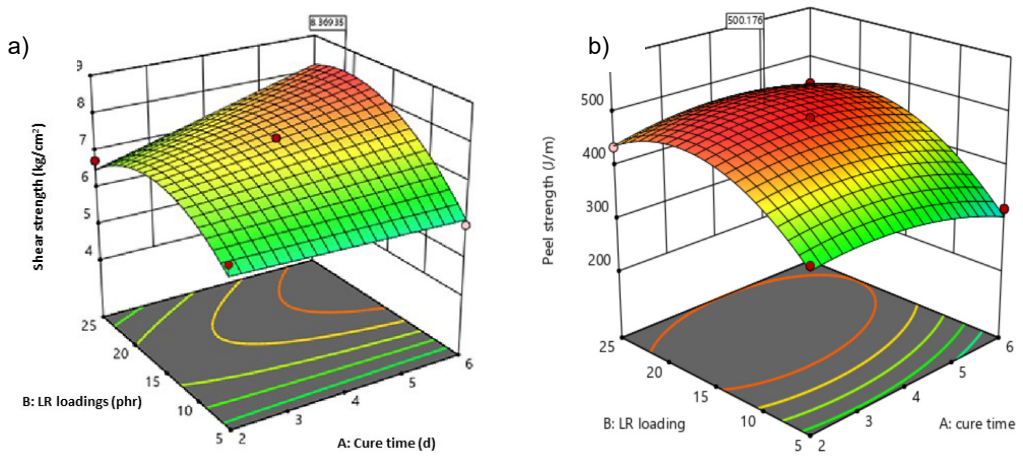

Figure 1: 3D- response plot for (a) shear strength and (b) peel strength

4. Conclusion

Optimization of the curing conditions is done by analyzing the response plots as well. The mix and match of past literature data for the DOE matrix in order to obtain the mathematical model for shear and peel strength is proven fruitful. This is because the adjusted coefficient of determination (R^2) values for both models are close to 1. The lack of fit test for both mathematical models are insignificant. The capability of both mathematical models to predict the shear and peel strength of LENR/Epoxy blend is validated using past literature that used ESR/epoxy system. The optimum conditions suggested by the software based on the response surface plots is 20.646 phr with a cure time of 6.94 d for shear strength and 18.441 phr with a cure time of 3.754 d for peel strength.

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