İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

EFFECTS OF EPOXY RESIN AND HARDENER TYPE ON DURABILITY AND MECHANICAL PROPERTIES OF EPOXY MIXES

M.Sc. Thesis By

Eren ÖZEREN

Department: Interdisciplinary

Programme: Polymer Science and Technology

Supervisor : Prof. Dr. Hulusi ÖZKUL

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PREFACE

I want to thank to my thesis supervisor Prof. Dr. Hulusi Özkul for his support , attention and contributions, to Sika Yapı Kimyasalları A.Ş. where I prepared my thesis, firstly to Ms. Nazmiye Parlak, to Dr.Ali Sağlam, to Mr. Barış Özer and to members of concrete and chemistry laboratories and finally to all members of Sika.

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TABLE OF CONTENTS

ABBREVATIONS .... **v**

LIST OF TABLES .... **vi**

LIST OF FIGURES .... **vii**

ÖZET .... **ix**

SUMMARY .... **xix**

1. INTRODUCTION **1**
  1.1 Epoxy 1
  1.2 History of the Epoxy Resin 3
  1.3 Recent Developments in Epoxy Resins 4
  1.4 Chemical Structure 4

2. ADDITIVES FOR EPOXY RESINS **14**
  2.1 Diluents 14
  2.2 Non-reactive Diluents 14
  2.3 Reactive Diluents 15
  2.4 Epoxy-based Reactive Diluents 15
  2.5 Non-epoxy Based Reactive Diluents 16
  2.6 Fillers 17
  2.7 Flexibilisers 17
  2.8 Curing Agents 18
    2.8.1 Nitrogen-containing Curing Agents 19
    2.8.2 Oxygen-containing Curing Agents 20
    2.8.3 Sulphur-containing Curing Agents 21
  2.9 Curing Agents Used in This Study 22
    2.9.1 2,2,4- 2,4,4 Trimethyl-hexamethylene Diamine (TMD) (Hardener 1) . 22
    2.9.2 -Trimethylhexamethylene diamine, cyanoethylated mixture of isomers (trimethylhexane -1,6-diamine) (Hardener 4) 23
    2.9.3 Tertiary amine (2,4,6 tris di methyl aminomethyl phenol) (Hardener 6) 24
    2.9.4 Triethylene tetra amine (Hardener 3) 24
    2.9.5 Meta-xylenediamine (Hardener 2) 25
    2.9.6 Isophorane diamine (xylenediamine) (Hardener 5) 26
  2.10 Structure and properties of cured resins 27

3. APPLICATIONS FOR EPOXY 28
- 3.1 General Applications for Epoxy Resins 29
  - 3.1.1 Epoxy in Civil Engineering 29
    - 3.1.1.1 Flooring 30
    - 3.1.1.2 Road and bridge coatings 31
    - 3.1.1.3 Concrete bonding and repair 32

4. EXPERIMENTAL PART 34
- 4.1 Materials 34
  - 4.1.1 Epoxy Resins 34
  - 4.1.2 Hardeners 35
  - 4.1.3 Reactive Diluent 35
  - 4.1.4 Aggregate 35
  - 4.1.5 Benzyl Alcohol
- 4.2 Rheological Measurements 36
  - 4.2.1 Viscosity measurements 36
  - 4.2.2 Flow table measurements 37
- 4.3 Epoxy content 39
- 4.4 Pot-life 40
- 4.5 Hardened State Measurements 42
  - 4.5.1 Bending (Flexural) and Compressive Strength 42
  - 4.5.2 Durability-Chemical resistance tests 44
  - 4.5.3 Pull-off Adhesion Test 45

5. RESULTS AND DISCUSSION 50
- 5.1 Rheological Measurements 50
  - 5.1.1 Viscosity 50
  - 5.1.2 Flow Table Measurements 52
- 5.2 Pot –life 57
- 5.3 Hardened State Measurements 61
  - 5.3.1 Bending and compressive strength 61
  - 5.3.2 Durability-Chemical Resistance 67
- 5.4 Pull-off Adhesion Test 70

6. CONCLUSION 75
- 6.1 Conclusions On Rheological Properties 75
  - 6.1.1 Viscosity and flow –table 75
- 6.2 Pot-life 75
- 6.3 Conclusions for Hardened State Measurements 77
  - 6.3.1 Bending (flexural) and compressive strength 77
  - 6.3.2 Durability-Chemical resistance 79
- 6.4 Pull-off Adhesion Test 80
- 6.5 General Evaluation 80

REFERENCES 82

APPENDIXES 84

Curriculum Vitae 106

ABBREVIATIONS

Bis : Bisphenol
RA : Bisphenol A resin
RF : Bisphenol F resin
RFA : The mixture of 70 % bisphenol A resin and 30 % bisphenol F resin
DGEBA : Diglycidyl ether of bisphenol A
Hr 1 : Hardener 1, TMD, 2,2,4- 2,4,4 Trimethyl-hexamethylene Diamine
Hr 2 : Hardener 2, Meta-xylenediamine
Hr 3 : Hardener 3, TETA, Triethylene tetra amine
Hr 4 : Hardener 4, Trimethylhexamethylene diamine, cyanoethylated mixture of isomers (trimethylhexane -1,6-diamine)
Hr 5 : Hardener 5, IPDA, Isophorane diamine (xylenediamine)
Hr 6 : Hardener 6, 2,4,6 tris di methyl aminomethyl phenol
R : Reference

LIST OF TABLES **Page No**

Table 2.1 Advantages and disadvantages of filler incorporation 17
Table 2.2 Estimated world market for curing agents by type 20
Table 2.3 Beneficial and negative properties of most common curing agent types 21
Table 4.1 General information about epoxy resins used in this study 34
Table 4.2 General properties of the hardeners used in this study 35
Table 4.3 Properties of reactive diluents used in this study 35
Table 4.4 The quantities of hardeners per 100g resin that are used in this study . 41
Table 4.5 Chosen samples for chemical resistance test 45
Table 5.1 Viscosity values of epoxy resins with 10% addition of various reactive diluent types 50
Table 5.2 Viscosities of resin mixtures 51
Table 5.3 Flow table measurements 54
Table 5.4 Pot-life results of the samples with different hardeners and reactive diluents 58
Table 5.5 Pot-life results of the samples 59
Table 5.6 Bending and compressive strength results for 1 day samples 64
Table 5.7 Bending and compressive strength results for 14 day of samples 65
Table 5.8 Results of chemical resistance test 68
Table 5.9 Pull-off test results showing the adhesion strength f_h 71
Table A.1 General test results for samples R1-R18 with hardener 3 85
Table A.2 Experiment results of mixtures containing hardener 6 86
Table A.3 Experiment results of given samples 87
Table C.1 Photographs of the samples left in alcohol for 1 and 21 days 92
Table C.2 Photographs of the samples left in 37% formaldehyde solution for 1 and 21 days 93
Table C.3 Photographs of the samples left in 15% lactic acid solution for 1 and 21 days 94
Table C.4 Photographs of the samples left in 20% formic acid solution for 1 and 21 days 95
Table D.1 1 day bending and compressive strength results of the sampes including HR3 96
Table D.2 14 day bending and compressive strength results of the sampes including HR3 98
Table D.3 1 day bending and compressive strength results of the sampes including HR6 100
Table D.4 14 day bending and compressive strength results of the sampes including HR6 102
Table D.5 1 day bending and compressive strength results of the sampes including RRDF 104
Table D.6 14 day bending and compressive strength results of the sampes including RRDF 105

LIST OF FIGURES **Page No**

Figure 1.1 : Idealised chemical structure of a simple epoxy (Ethylene Oxide)..... 1
Figure 1.2 : Idealised chemical structure of a typical epoxy of the ester 2
Figure 1.3 : Catalyst of Bisphenol A 6
Figure 1.4 : Formation of epichlorohydrin 7
Figure 1.5 : Low molecular weight prepolymer which is containing reactive epoxy groups 8
Figure 1.6 : Chemical structure of bisphenol F 9
Figure 1.7 : Epoxy-Novolac resins 9
Figure 1.8 : The scheme for cure of epoxy resins..10
Figure 1.9 : Curing mechanism of an amine type hardener...................................10
Figure 1.10 : Cross-linking of epoxy prepolymer 11
Figure 1.11 : Cross-linking of prepolymer by using polyanhydrides......................12
Figure 2.1 : 2,2,4- 2,4,4 Trimethyl-hexamethylene Diamine (TMD)....................22
Figure 2.2 : Chemical structure of TETA..25
Figure 2.3 : Chemical structure of IPDA...26
Figure 4.1 : LVT Brookfield Viscometer 37
Figure 4.2 : 798 MPT Titrino titrometer...39
Figure 4.3 : Schematic show of flexural loading...43
Figure 4.4 : Samples in oiled dies..43
Figure 4.5 : Alşa Laboratory Equipment on which the bending and compression tests were made 43
Figure 4.6 : Plan of specimen for pull-off test, showing dolly locations and cross section of test plate 47
Figure 4.7 : Nature of the failures shown on the scheme 49
Figure 5.1 : Viscosity change upon functionality of reactive diluents with 10% reactive diluent addition..51
Figure 5.2 : Viscosity change of Bisphenol A resin with different quantities of monofunctional reactive diluent addition 52
Figure 5.3 : Viscosities of pure samples and flow table values of hardener 3 added versions of same mixes..53
Figure 5.4 : Viscosity and flow ratio relation of samples including hardener 6....55
Figure 5.5 : Viscosity and flow ratio relation of samples including hardener.......55
Figure 5.6 : Comparison of flow table results with the formula given above, for the samples including Hr 3..56
Figure 5.7 : Comparison of flow table results of the hardeners and the mixtures with 10% monofunctional reactive diluent addition...........................56
Figure 5.8 : Pot-life comparison between hardener types for bisphenol a resin with different reactive diluent additions.................................60
Figure 5.9 : Pot-life comparison of different resin mixtures with addition of various rates of reactive diluents...60

Figure 5.10 : Pot-life comparison for hardener 6 mixtures with different resin types. 61
Figure 5.11 : Pot-life comparison for hardener 3 mixtures with different resin types 61
Figure 5.12 : 1 day bending results of samples with different hardener and reactive diluent types 66
Figure 5.13 : 1 day bending test results of resins with Hr 3 and Hr 6 66
Figure 5.14 : 1 day compression test results of resins with Hr 3 and Hr 6 67
Figure 5.15 : Adhesion strength comparison according to hardener type used 72
Figure 5.16 : Adhesion strength change with various rates of reactive diluent addition....73
Figure 5.17 : Effect of diluent type on adhesion strength of resin A and hardener 3....73
Figure 5.18 : Performances of mixtures including hardener 3....74
Figure 6.1 : Sample including hardener 4 and 30% benzyl alcohol, after compression 78
Figure B.1 : 1 day compressive test results of samples with different hardeners and reactive diluents....88
Figure B.2 : 14 day bending test results of samples with different hardeners and reactive diluents....88
Figure B.3 : 14 day compressive test results of samples with different hardeners and reactive diluents 89
Figure B.4 : 1 day bending test results of the given mixtures with hardener 3 and hardener 6....89
Figure B.5 : 1 day compressive test results of the given mixtures with hardener 3 and hardener 6....90
Figure B.6 : 14 day bending test results of the given mixtures with hardener 3 and hardener 6....90
Figure B.7 : 14 day compressive test results of the given mixtures with hardener 3 and hardener 6....91

EPOKSİ KARIŞIMLARINDA EPOKSİ REÇİNESİ VE SERTLEŞTİRİCİ TİPİNİN DURABİLİTE VE MEKANİK ÖZELLİKLERİ ÜZERİNE ETKİLERİ

ÖZET

Epoksi kelimesi, dışından bağlanan anlamına gelen “epi” ve oksijenin kısaltması olan “oksi” kelimelerinin bileşiminden oluşmaktadır. Yani epoksi kelimesi, dışından bağlanan oksijen anlamına gelmektedir.

İlk bölümde , epoksi reçineleri tanıtılmıştır. Reçine çeşitleri, epoksinin tarihi, yakın zamandaki gelişmeler, kimyası, reçine özellikleri ve kür işlemi anlatılmıştır.

Epoksinin düşük viskozite, kolay işlenebilirlik, 5°C - 150°C arasında hızlı kür alma, yüksek kimyasal ve mekanik dayanım, iyi yapışma, iyi elektriksel özellikler, kür sonrası boyutlarda küçülmenin az olması gibi pek çok avantajlı özelliği vardır. Bu nedenle epoksi reçineleri genellikle diğer pek çok reçineye tercih edilir.

İkinci bölümde, epoksi reçineleri için katkı maddeleri olan seyrelticiler, dolgular, fleksibilizerler ve kür ajanları anlatılmıştır. Tipleri ve özellikleri açıklanmıştır. Kullanılan kür ajanlarının yapıları ve özellikleri detaylarıyla verilmiştir.

Yapısına bakıldığında epoksi grubunun iki karbon atomuna bağlanmış oksijenden oluştuğu görülür. Basit bir yapıya sahip olmakla birlikte epoksi çok önemli bir malzemedir. Neredeyse her sektörde kullanılan epoksinin bazı kullanım alanları kompozit malzemeler, döküm bileşikleri, yağlayıcılar, cilalar, boyalar, yapıştırıcılar, havacılık uygulamaları, model malzemeleri, optik ve elektriksel uygulamalar ve tabi ki inşaat sektörüdür. Üçüncü bölümde epoksinin kullanım alanları, özellikle inşaat sektöründeki kullanımı detaylarıyla açıklanmıştır.Bu sektördeki kullanımı da yer kaplamaları, yol ve köprü kaplamaları, beton bağlama ve onarım gibi başlıklarda toplanabilir.

Temel epoksi reçinesi Bisfenol A olmakla birlikte Bisfenol F, epoksi –novalak reçineleri gibi diğer epoksi reçineleri de mevcuttur. Sertleştirici ki kürlenmiş reçinenin ikincil bileşenidir (birinci bileşen reçinenin kendisidir), seyreltici gibi katkı malzemeleri dayanım özelliklerini etkiler. Bu durum özellikle beton karışımları için geçerlidir. Bu çalışmada epoksi reçinesi, sertleştirici ve reaktif seyreltici seçiminin bazı fiziksel ve mekanik özellikler üzerine etkisi araştırılmıştır.

Dördüncü bölümde, kullanılan malzemelerin özellikleri detaylarıyla verilmiş ve test metodları açıklanmıştır. Bu çalışmada yapılmış olan testler reolojik özellikler başlığında viskozite ve yayılma ölçümleri olup, bunun dışında epoksi içeriği ve pot-life ölçümleri de bu çalışmada yer almaktadır. Sertleştirilmiş durumdaki ölçümler eğme-basma, yapışma ve kimyasal dayanım deneylerini içerir. Ölçümlerin ilk kısmında saf reçine veya kürlendirilmemiş reçine karışımları kullanılmıştır, ikinci kısımdaysa eğme - basma deneylerinde ve kimyasal dayanımda reçine ve kum

karışımları yani epoksi karışımı içeren beton, yapışma testindeyse reçine ve sertleştirici karışımı kullanıldı.

Beşinci bölümde deney sonuçları ilgili tablo ve grafiklerle birlikte verilmiştir. Önce viskozite değişimi farklı seyreltici oranları ve tipleriyle verilmiştir.

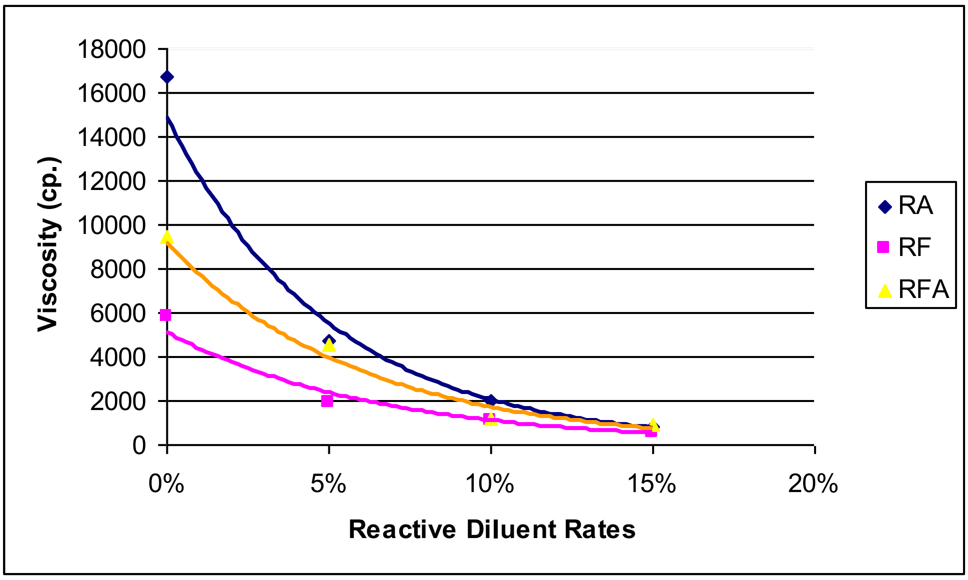
Tablo1'de viskozite sonuçları farklı seyreltici oranlarıyla verilmiştir.

Tablo 1: Farklı seyrelticilerin %10 ilavesiyle elde edilmiş viskozite değerleri**.**

Fonksiyonellik	Reçine tipi ve viskozite (cp.)		
	RA	RF	RFA
10 % monofunc.	2000	1100	1150
10 % difunct.	2600	1200	2400
10 % trifunct.	3700	2800	3200

Yukarıda görüldüğü gibi mono-fonksiyonel seyrelticiler viskozite düşürmedi di-fonksiyonel ve trifonksiyonel seyrelticilerden daha etkili, di-fonksiyonel seyrelticiler de tri-fonksiyonellerden daah etkilidir.

Aşağıda figure 1 seyreltici katkısı oranının viskoziteye etkisini göstermektedir.

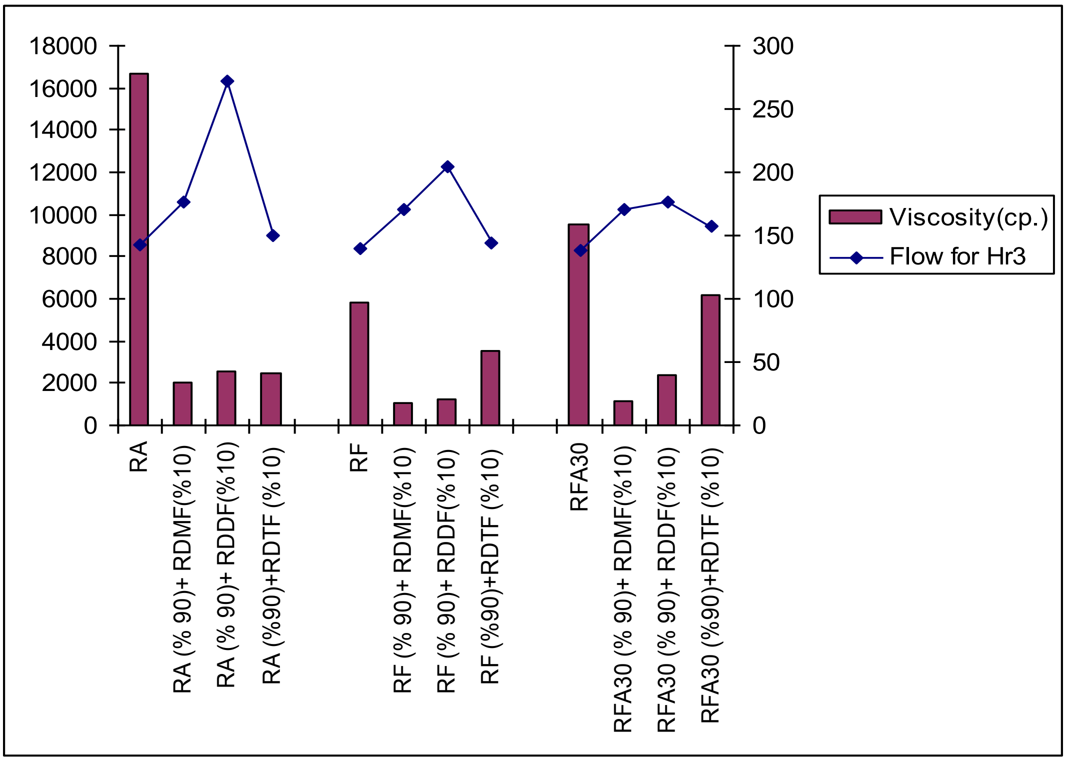


Figür 1: Farklı oranlarda mono-fonksiyonel seyreltici katkısının reçine viskozitesine etkisi.

Seyreltici oranı arttıkça viskozite azalmaktadır.

Akma sonuçları viskozite ile negatif korelasyona sahiptir. Viskozite arttıkça akma azalır. Aktivatör katkısı ve sertleştirici miktarı da akmayı etkileyen faktörlerdir.

Figür 2 sertleştirici 3 için saf reçinenin viskozite ve akma değerlerini göstermektedir.

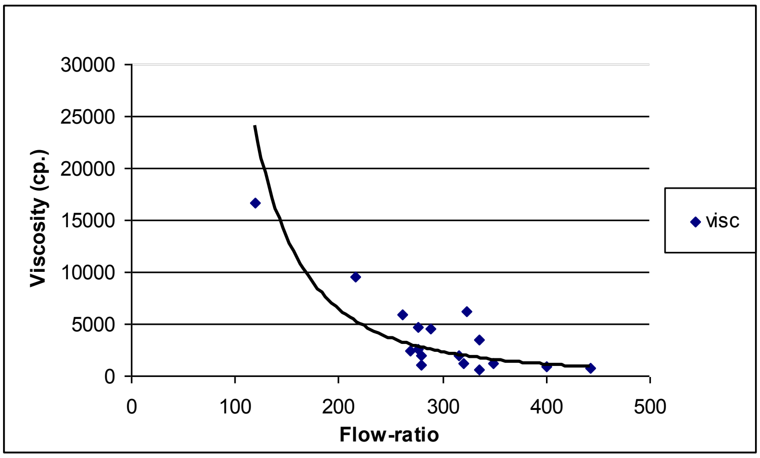


Figür 2: Saf reçine ve sertleştirici 3 eklenmiş örneklerin viskozite ve akma sonuçları.

Malzemelerin akma değerleri akma-oranıyla da incelenebilir. Bu değerin hesaplanması aşağıdaki (1) numaralı formülle olur.

$$\psi = \frac{A - A_0}{A_0} \qquad (1)$$

Figür 3, viskozite ve akma arasındaki negative ilişkiyi sertleştirici 6 içeren numunelerle göstermektedir.



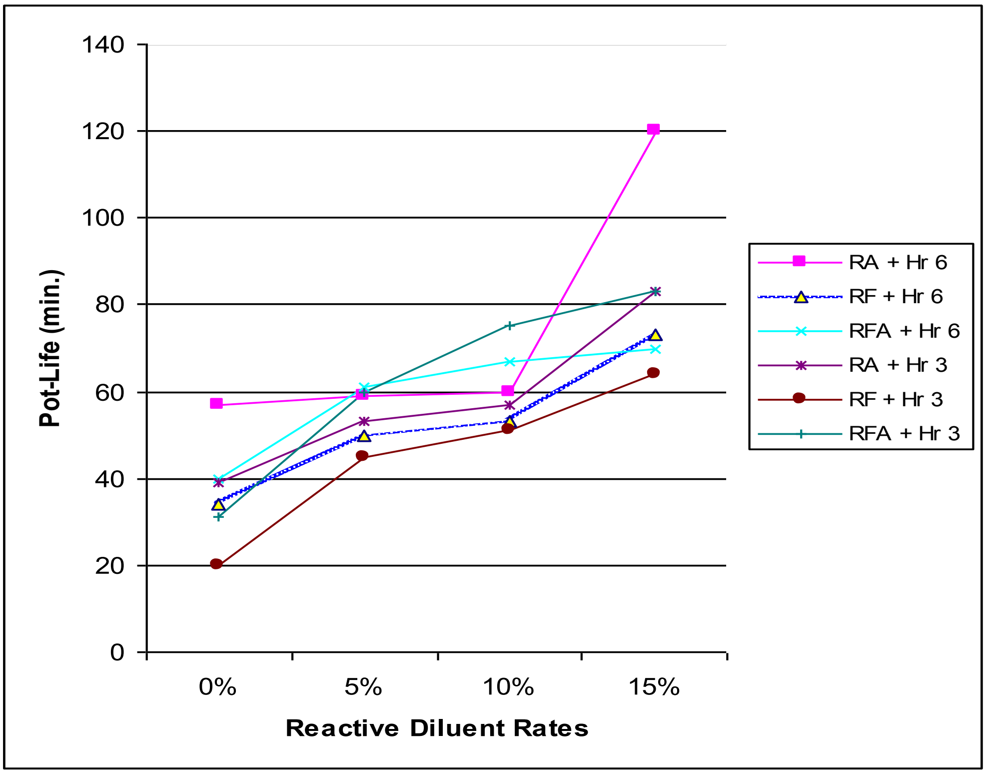
Figür 3: Sertleştirici 6 içeren numuneler için viskozite ve akma ilişkisi.

Pot-life testi çok sayıda numuneye uygulanmıştır. Esas deneylere başlanmadan önce optimum pot-life sonuçlarına ulaşabilmek ve optimum sertleştirici miktarını ede etmek için bir çok deneme yapılmıştır. Hr 4 ve Hr 5 sertleştiricilerinin performansını arttırabilmek için benzil alkol kullanılmıştır. %10 aktivatör ilavesi Hr 5 için yeterliyken, bu oran Hr 4 için %30 olmuştur.

Sertleştirici tipine göre pot-life'lar karşılaştırılırsa aşağıdaki gibi bir sıralama elde edilir;

Hr 3 < Hr 1< Hr 5 + 10 %Act.< Hr 6 < Hr 4 + 30 % Act.< Hr 2 <Hr 5 < Hr 4 .

Seyreltici miktarı arttıkça pot-life da artar. Bu sonuç Figür 4'te görülmektedir.



Figür 4: Çeşitli reçine karışımlarının değişik seyreltici oranlarıyla pot-life karşılaştırması.

Seyrelticiler karşılaştırılırsa RDDF'nin en kısa pot-lifeı verdiği, bununla birlikte genellikle RDTF'nin en uzun pot-life değerini verdiği görülür.

Eğme ve basınç testleri hem 1 hem de 14 günlük uygulanmıştır. Eğme içi uygulanan yük 2kN, basınç için uygulanan yük 25kN'dur. Sertleştirici performansları aşağıdaki gibidir;

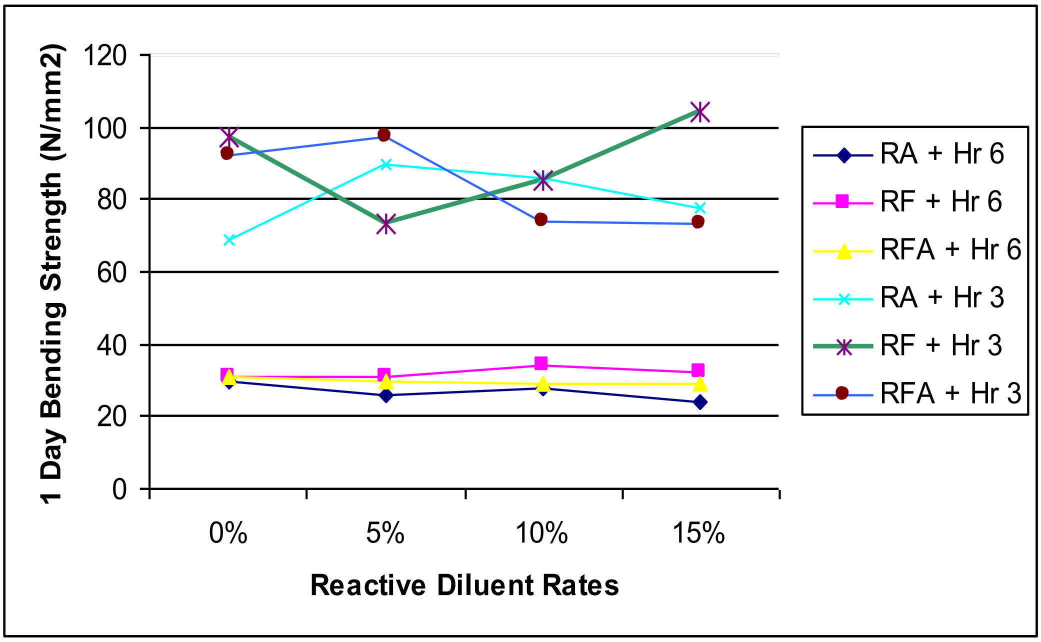
Hr 3 > Hr 4 > Hr 1 > Hr 2 > Hr 5+10% Act .> Hr 6 >Hr 5 > Hr 4+30% Act.

Seyreltici performansları karşılaştırılırsa, numuneden numueye değişebilmekle birlikte, genellikle RDDF daha iyi sonuçlar vermiştir. RDTF''nin de performansı iyidir ancak RDMF daha düşük sonuçlar göstermiştir.

Tablo 2 ve 3 numunelerin 1 ve 14 günlük dayanım değerlerini göstermektedir. Hr 4 için sonuçlar aktivatör kullanılmamış numuneler için daha iyidir. Bununla birlikte, Hr 5 için aktivatör kullanımı dayanımı arttırmıştır.

Reçine performansları karşılaştıtılacak olursa, sonuçların çok ayırt edici olmadığı görülür. Ancak genellikle RFA30 ve RF reçineleri RA'dan daha iyi sonuç vermiştir.

Şekil 5, Hr 3 ve Hr 6 içeren numunelerin 1 günlük eğilme testi sonuçları göstermektedir. Burda Hr 3'ün dayanımının Hr 6'dan çok daha iyi olduğu görülür.



Figür 5: 1 day bending test results of resins with Hr 3 and Hr 6.

Kimyasal dayanım testi için epoksi üzerinde en etkili olan çözeltiler kullanılmıştır, bunlar alkl, %37 formaldehit, %15 laktik asit ve %20 formik asit çözeltileridir.
Genel olarak bütün numuneler alkol ve formaldehite karşı dayanımlıyken, test süresi sonuna asitlerden hasar görmemiş numune kalmamıştır. Hasarın boyutu ise numunenin performansına bağlıdır. Kimyasal dayanım testi sonuçları Tablo 4'te verilmiştir. Tablo üzerindeki harflerin anlamları şöyledir;

A- Hasarsız
B- Düşük hasa
C- Orta hasar
D- Renk solması
E- Şiddetli hasar

Tablo 2: 1 günlük numunelerin eğilme basınç dayanımı sonuçları

Reçine Karışımı	Eğilme day. (N/mm2)	Basınç day. (N/mm2)	Reçine Karışımı	Eğilme day. (N/mm2)	Basınç day. (N/mm2)
RFA30+HR 6	8,25	30,19	RFA30 + HR 3	24,59	83,73
RA+HR 6	7,9	41,59	RA + HR 3	18,53	75,94
RF+HR 6	8,32	40,46	RF + HR 3	25,95	79,74
RFA30 (% 90)+ RDMF(%10) +HR 6	7,75	32,25	RFA30 (% 90)+ RDMF(%10) +HR 3	19,64	46,38
RFA30 (% 90)+ RDDF(%10) +HR 6	8,43	39,6	RFA30 (% 90)+ RDDF(%10) +HR 3	26,95	89,18
RFA30 (%90)+RDTF (%10) +HR 6	8,17	42	RFA30 (%90)+RDTF (%10) +HR 3	25,96	71,75
RA (% 90)+ RDMF(%10) +HR 6	7,49	38,85	RA (% 90)+ RDMF(%10) +HR 3	22,9	59,99
RA (% 90)+ RDDF(%10)+ HR 6	8,31	41,65	RA (% 90)+ RDDF(%10) +HR 3	25,29	80,03
RA (%90)+RDTF (%10) + HR 6	6,67	40,26	RA (%90)+RDTF (%10) +HR 3	30,48	87,92
RF (% 90)+ RDMF(%10) +HR 6	9,12	45,37	RF (% 90)+ RDMF(%10) +HR 3	22,65	49,15
RF (% 90)+ RDDF(%10) + HR 6	9,22	44,1	RF (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RF (%90)+RDTF (%10) +HR 6	8,69	46,98	RF (%90)+RDTF (%10) +HR 3	27,64	71,64
RFA(%95)+RDMF (%5) +HR 6	7,93	37,41	RFA30 (%95)+RDMF (%5)+HR 3	25,96	80,89
RFA(%85)+ RDMF (%15) +HR6	7,8	38,5	RFA(%85)+ RDMF (%15) +HR 3	19,42	44,37
RA (%95)+RDMF (%5) + HR 6	7,01	35,47	RA (%95)+RDMF (%5) +HR 3	24,11	81,87
RA(%85)+RDMF (%15) +HR 6	6,49	37,48	RA(%85)+RDMF (%15) +HR 3	20,72	50
RF(%95)+RDMF (%5) +HR 6	8,37	41,1	RF(%95)+RDMF (%5) +HR 3	19,4	41,3
RF(%85)+RDMF (%15)+HR 6	8,52	39,66	RF(%85)+RDMF (%15) +HR 3	27,67	77,88
RA + HR 2	12,49	75,17	RA + HR 5	4,5	26,39
RA+RDMF (10%) + HR 2	22,06	63,84	RA+RDTF (10%) + HR 5	5,49	33,32
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	20,26	83,03	RA+RDMF (10%) +HR 5	5,32	28,13
RA + HR 1	10,05	40,10	RA +HR 5+ 10%Act.	7,81	44,2
RA+RDMF (10%) + HR 1	22,1	44,17	RA+RDMF(10%)+HR 5+10%Act.	19,22	53,07
RA +RDDF (10%)+ HR 1	24,97	56,63	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	20,11	46,06	RA+RDTF (10%)+HR 5+10%Act.	23,66	68,92
RA (100) +HR 4	22,25	39,63	RA (100)+ HR 4+ 30% Act.	6,12	10,43
RA+RDMF (10%)+HR 4	23,22	42,36	RA+RDMF (10%)+ HR 4+ 30% Act.	1,71	2,76
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	25,72	54,12	RA+RDTF (10%)+ HR 4+ 30% Act.	3,79	6,35

Tablo 3: 14 günlük numunelerin eğilme basınç dayanımı sonuçları

Reçine Karışımı	Eğilme day. (N/mm2)	Basınç day. (N/mm2)	Reçine Karışımı	Eğilme day. (N/mm2)	Basınç day. (N/mm2)
RFA30+HR 6	10,64	56,57	RFA30 + HR 3	26,38	97,00
RA+HR 6	6,4	41,24	RA + HR 3	26,71	97,21
RF+HR 6	10,83	58,55	RF + HR 3	26,89	93,08
RFA30 (% 90)+ RDMF(%10) +HR 6	12,96	68,6	RFA30 (% 90)+ RDMF(%10) +HR 3	23,69	78,18
RFA30 (% 90)+ RDDF(%10) +HR 6	13,32	67,57	RFA30 (% 90)+ RDDF(%10) +HR 3	30,69	103,73
RFA30 (%90)+RDTF (%10) +HR 6	9,71	51,54	RFA30 (%90)+RDTF (%10) +HR 3	29,33	90,87
RA (% 90)+ RDMF(%10) +HR 6	9.68	57,31	RA (% 90)+ RDMF(%10) +HR 3	23,33	62,74
RA (% 90)+ RDDF(%10)+ HR 6	8,82	43,69	RA (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RA (%90)+RDTF (%10) + HR 6	9,43	48,54	RA (%90)+RDTF (%10) +HR 3	28,04	98,34
RF (% 90)+ RDMF(%10) +HR 6	12,04	64,63	RF (% 90)+ RDMF(%10) +HR 3	20,99	58,76
RF (% 90)+ RDDF(%10) + HR 6	14,22	78,86	RF (% 90)+ RDDF(%10) +HR 3	29,14	95,24
RF (%90)+RDTF (%10) +HR 6	12,2	71,85	RF (%90)+RDTF (%10) +HR 3	27,82	76,42
RFA(%95)+RDMF (%5) +HR 6	10,68	52,53	RFA30 (%95)+RDMF (%5)+HR 3	23,76	71,99
RFA(%85)+ RDMF (%15) +HR6	12,72	60,15	RFA(%85)+ RDMF (%15) +HR 3	21,69	58,27
RA (%95)+RDMF (%5) + HR 6	9,3	47,87	RA (%95)+RDMF (%5) +HR 3	23,3	74,05
RA(%85)+RDMF (%15) +HR 6	12,24	63,87	RA(%85)+RDMF (%15) +HR 3	19,29	56,12
RF(%95)+RDMF (%5) +HR 6	14,91	73,18	RF(%95)+RDMF (%5) +HR 3	22,7	62,2
RF(%85)+RDMF (%15)+HR 6	19,78	80,77	RF(%85)+RDMF (%15) +HR 3	19,48	48,79
RA + HR 2	16,07	82,01	RA + HR 5	5,62	32,25
RA+RDMF (10%) + HR 2	18,08	58,16	RA+RDTF (10%) + HR 5	6,02	35,18
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	23,36	77,78	RA+RDMF (10%) +HR 5	6,18	30,69
RA + HR 1	17,77	43,46	RA +HR 5+ 10%Act.	9,58	45,62
RA+RDMF (10%) + HR 1	19,21	41,43	RA+RDMF(10%)+HR 5+10%Act.	10,35	47,26
RA +RDDF (10%)+ HR 1	24,97	56,93	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	22,04	47,21	RA+RDTF (10%)+HR 5+10%Act.	19,57	49,88
RA (100) +HR 4	24,17	53,68	RA (100)+ HR 4+ 30% Act.	5,36	7,54
RA+RDMF (10%)+HR 4	25,03	54,98	RA+RDMF (10%)+ HR 4+ 30% Act.	3,49	6,5
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	26,88	64,25	RA+RDTF (10%)+ HR 4+ 30% Act.	5,69	8,76

Aşağıdaki tablo 4’te kimyasal dayanım sonuçları verilmiştir.

Tablo 4: Kimyasal dayanım testi sonuları.

No.	Kimyasal	1.hafta	2.hafta	3.hafta	1.hafta	2.hafta	3.hafta	Kimyasal	No.
1	Formald.	A	A	B	A	A	A	Formald.	9
	Alkol	A	A	A	A	A	A	Alkol	
	Formik A	C	E	E	C	C	C	Formik A	
	Lactik A	C	C	E	C	C	C	Lactik A	
2	Formald.	A	A	A	A	A	A	Formald.	10
	Alkol	A	A	A	A	A	A	Alkol	
	Formik A	C	E	E	C	C	E	Formik A	
	Lactik A	C	C	E	C	C	C	Lactik A	
3	Formald.	A	A	A	A	A	A	Formald.	11
	Alkol	A	A	A	A	A	A	Alkol	
	Formik A	B	C	C	C	E	E	Formik A	
	Lactik A	B	C	C	C	C	E	Lactik A	
4	Formald.	A	A	A	A	A	A	Formald.	12
	Alkol	A	A	A	A	A	B	Alkol	
	Formik A	A	C	C	E	E	E	Formik A	
	Lactik A	B	C	C	E	E	E	Lactik A	
5	Formald.	A	A	A	A	A	A	Formald.	13
	Alkol	A	A	A	A	A	A	Alkol	
	Formik A	C	C	C	C	C	C	Formik A	
	Lactik A	B	B	C	C	E	E	Lactik A	
6	Formald.	A	A	A	A	A	A	Formald.	14
	Alkol	A	A	A	A	B	B	Alkol	
	Formik A	E	E	E	C	E	E	Formik A	
	Lactik A	C	E	E	E	E	E	Lactik A	
7	Formald.	A	A	A	A	A	A	Formald.	15
	Alkol	A	A	A	A	A	A	Alkol	
	Formik A	A	B	B	C	E	E	Formik A	
	Lactik A	A	B	B	B	E	E	Lactik A	
8	Formald.	A	A	A	A	A	A	Formald.	R
	Alkol	A	A	B	A	A	A	Alkol	
	Formik A	E	E	E	B	C	C	Formik A	
	Lactik A	E	E	E	B	C	C	Lactik A	

Tablo RA’nın performansının diğer reçinelerden daha iyi olduğunu gösterir. RF ve RFA30 reçinesi yaklaşık aynı dayanıma sahiptir ancak RF formaldehitten de zarar görmütür. Bu karışım formaldehitten zarar görmüş tek karışımdır.

Hr.3 ve Hr1 iyi performans göstermiş sertleştiricilerdir, Hr 3 içeren karışım Hr 1 içerene kıyasla asit çözeltilerinde bozulmaya 1 hafta daha geç başlamıştır. Hr 2 de neredeyse Hr 1 ile ayı performansa sahiptir. Hr 5 ise en kötü sonuçları vermiştir. Test süresi sonunda Hr 5 ile yaklaşık aynı sonucu vermiş numuneler bulunmaktadır ancak Hr 5 bunlardn daha önce bozulmaya başlamıştır. Ayrıca performans azalan seyreltici oranıyla artmaktadır. Bu da eğme-basma deneyindekine paralel bir sonuçtur.

Seyrelticinin fonksiyonelliği de sonucu etkiler, RDTF içeren numuneler genellikle en iyi sonucu vermişken, en düşük sonuçlar RDDF ile elde edilmiştir.

Polar hidroksil ve eter gruplarının varlığı, epoksi reçinesine mükemmel yapışabilme özelliği verir. Reçine düşük çekme ile kür alır, sonuçta reçine ve yapışan madde arasnda çeşitli yüzey bağlantıları kurulur.Tablo 5 pull-off sonuçlarını göstermektedir.

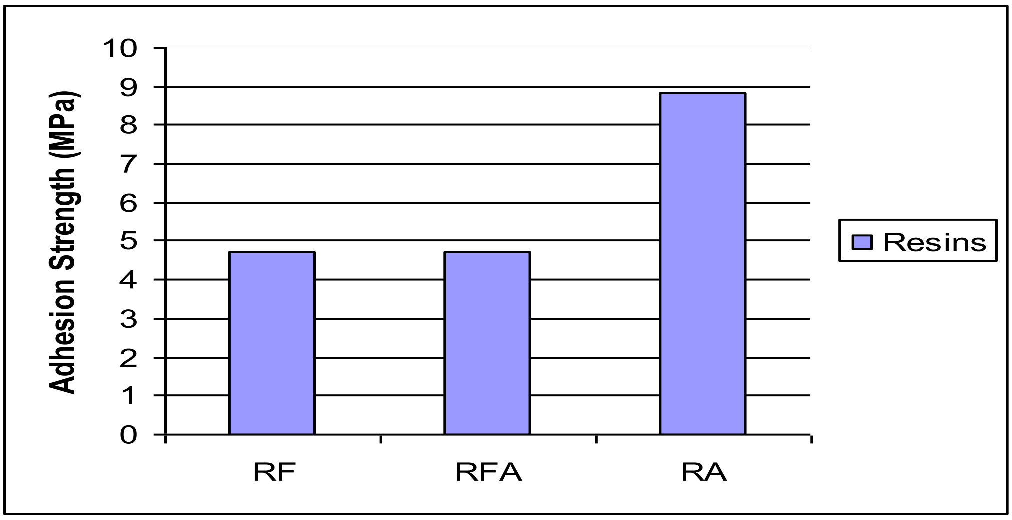
Tablo 5: Pull-off test sonuçları.

Örnek	1. değer (MPa)	2.değer (MPa)	3. değer (MPa)	f_h (MPa)
RF + Hr.3. + kum	5,12	4,64	4,40	4,72
Kopma yüzeyi	A	-/Y	-/Y	
RFA30 + Hr.3.+ kum	4,70	5,06	4,34	4,70
Kopma yüzeyi	-/Y	A	-/Y	
RA +Hr.3 +kum	8,52	9,12	-	8,82
Kopma yüzeyi	A	A	A	
RA (%95) + RDMF (%5)+ Hr.3 + kum	4,17	3,20	3,60	3,66
Kopma yüzeyi	-/Y	Y	Y	
RA (%90) + RDMF (%10)+ Hr.3 + kum	3,42	2,17	2,45	2,68
Kopma yüzeyi	-/Y	Y	Y	
RA (%90) + RDDF (%10)+ Hr.3 +kum	5,02	3,58	5,86	4,82
Kopma yüzeyi	-/Y	Y	A	
RA (%90) + RDTF (%10)+ Hr.3 + kum	4,96	4,42	4,66	4,68
Kopma yüzeyi	-/Y	-/Y	-/Y	
RA (%85) + RDMF (%15)+ Hr.3 + kum	2,78	3,74	3,56	3,36
Kopma yüzeyi	Y	-/Y	-/Y	
RA + Hr.1 + kum	5,64	3,40	5,09	4,71
Kopma yüzeyi	A	-/Y	-/Y	
RA + Hr.2 + kum	14,6	13,8	-	14,2
Kopma yüzeyi	A	A	A	
RA + Hr.4 + kum	2,96	4,02	4,27	3,75
Kopma yüzeyi	-/Y	B	B	
RA +Hr.5 + kum	2,02	1,96	3,64	2,54
Kopma yüzeyi	Y	Y	A/B	
RA + Hr.5 + % 10 Activator + kum	10,16	8,76	-	9,46
Kopma yüzeyi	A	A	A	
RA (%90) + RDDF (%10)+ Hr.5 + kum	5,80	4,22	3,24	4,42
Kopma yüzeyi	A	A/B	Y	
RA (%95) + RDTF (%5)+ Hr. 3 + kum	6,70	5,45	3,45	5,20
Kopma yüzeyi	A	A/B	-/Y	

Sertleştiricilerin performans sıralaması aşağıdaki gibidir.

Hr 2 >Hr 5+10% Activator > Hr 3 > Hr 1 > Hr 4 > Hr 5

Figür 6 hr 3 içeren numuneler için performans sıralamasını göstermektedir.



Figür 6 : Hr 3 içeren numuneler için reçine tipinin yapışmaya etkisi.

Seyreltici ilavesi performans düşürür. RDMF içn en yüksek sonuç e düşük seyreltici katkısıyla elde edilmiştir. Ancak %15 RDMF katılmış numuneler %10 RDMF katılmışlardan daha iyi sonuç vermiştir. Acak %5 RDMF katkısı bile performansı çok fazla düşürmüştür.

Bu çalışmaların ardından sonuç bölümünde, bu çalışmadan çıkan sonuçlar tartışıldı. Gözlemlenen en önemli sonuç reçine ve sertleştirici katkılarının betonda mekanik dayanımı çok büyük bir şekilde arttırdığıydı. Bu çalışma ayrıca epoksi reçineleriyle ilgili bilinenleri doğruladı.

EFFECTS OF EPOXY RESIN AN D HARDENER TYPE ON DURABILITY AND MECHANICAL PROPERTIES OF EPOXY MIXES

SUMMARY

The word epoxy comes from the bonding of two words “epi” which means “on the outside of” and the “oxy”, the shortened form of “oxygen”. Joined together these two words form describe the materials molecular structure; an oxygen atom that is located outside of two carbon atoms.

In the first chapter of the study, an introduction to the epoxy resins were made. Resin types, history of the epoxy resim, recent developments, chemistry and properties of the resins and cure process were told.

It has many advantageous properties like low viscosity, easily processability, quick cure between 5°C to 150°C , high chemical resistance and strength, good adhesion, good electrical properties, low shrinkage on curing. So epoxy resin is generally preferred rather than other resins.

In chapter two, additives for epoxy resins were told which are diluents, fillers, flexibilizers and curing agents. Their types and properties were explained. The used curing agents structures and properties were given with details.

Although it has a simple structure epoxy resin is a very important material. It finds many usages nearly in all industries, some applications are composites material, strain gage backings, sealants, casting compounds, varnishes, paints, laminating resins, adhesives, model materials, potting, encapsulation, aircraft components, some optical and electrical applications and surely in civil industries. In chapter three, applications of epoxy were given detailed, especially for civil industry. Flooring, road and bridge coatings and concrete bonding and repair are main objects in civil industry.

However the basic epoxy resin is considered as Bisphenol A, there are some other epoxy resin types such as Bisphenol F or novolac resins. Additional materials for epoxy resins like hardeners which is the secondary component of cured resin (first component is the resin itself) or reactive diluents affect the strength. This is especially valid for concrete mixes. In this study the effects of epoxy resin, hardener, reactive diluent choices on some rheological and mechanical properties were examined.

In chapter four, the details of used materials were given and test methods were explained. The tests applied in this study were rheological measurements including viscosity and flow-table,then epoxy-content and also pot-life measurements were included Hardened state measurements which depends on mechanical properties including bending and compressive strength tests , and also pull-off and chemical resistance tests. In the first part of measurements, pure resin or uncured resin mixtures are used, in the second part hardened epoxy resins which means concrete with epoxy resin, hardener and in some samples reactive diluent addition were used.

In chapter five, test results were given with related tables and graphics. First, viscosity change were given with different reactive diluent functionality and addition rates.

In the table 1 below, viscosity results of resins with different reactive diluent additons were given.

Table 1: Viscosity values of epoxy resins with 10% addition of various reactive diluent types

Functionality and quantity	Resin Type and Viscosity (cp.)		
	RA	RF	RFA
10 % monofunc.	2000	1100	1150
10 % difunct.	2600	1200	2400
10 % trifunct.	3700	2800	3200

As seen above, monofunctional reactive diluents were more effective for viscosity reduction than difunctional ones and difunctional reactive diluents were more effective than trifunctional reactive diluents.

And the figure 1 below shows the effect of reactive diluent addition rate in viscosity.

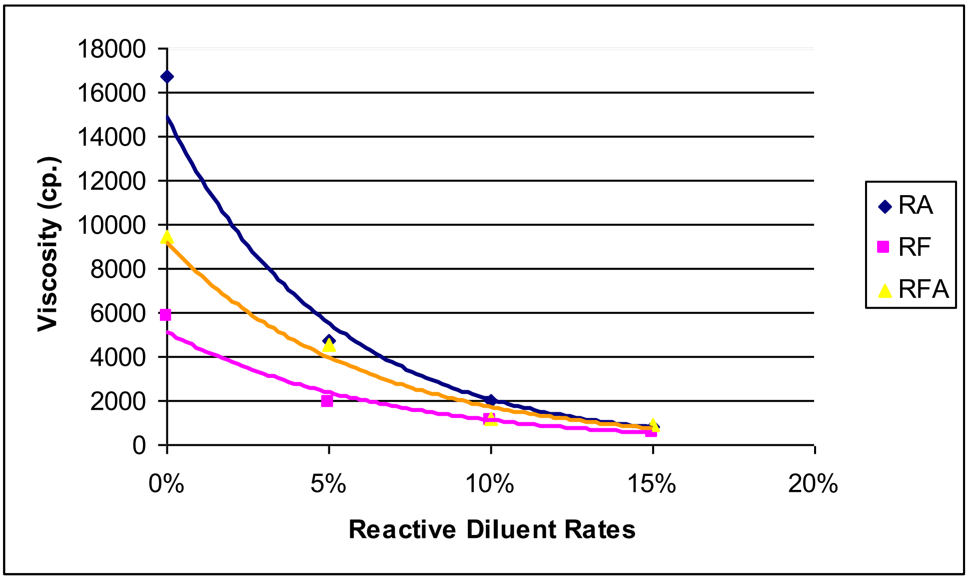


Figure 1: Viscosity change of resins with different quantities of monofunctional reactive diluent addition

As the rate of reactive diluent increases viscosity reduces.

Flow-table results shows a negative correlation with viscosity results. As the viscosity increases flow-table measurements decreases. Activator addition and hardener quantity also affects the viscosity.

Figure 2 shows viscosities of pure samples and flow table values of hardener 3 added versions of samples.

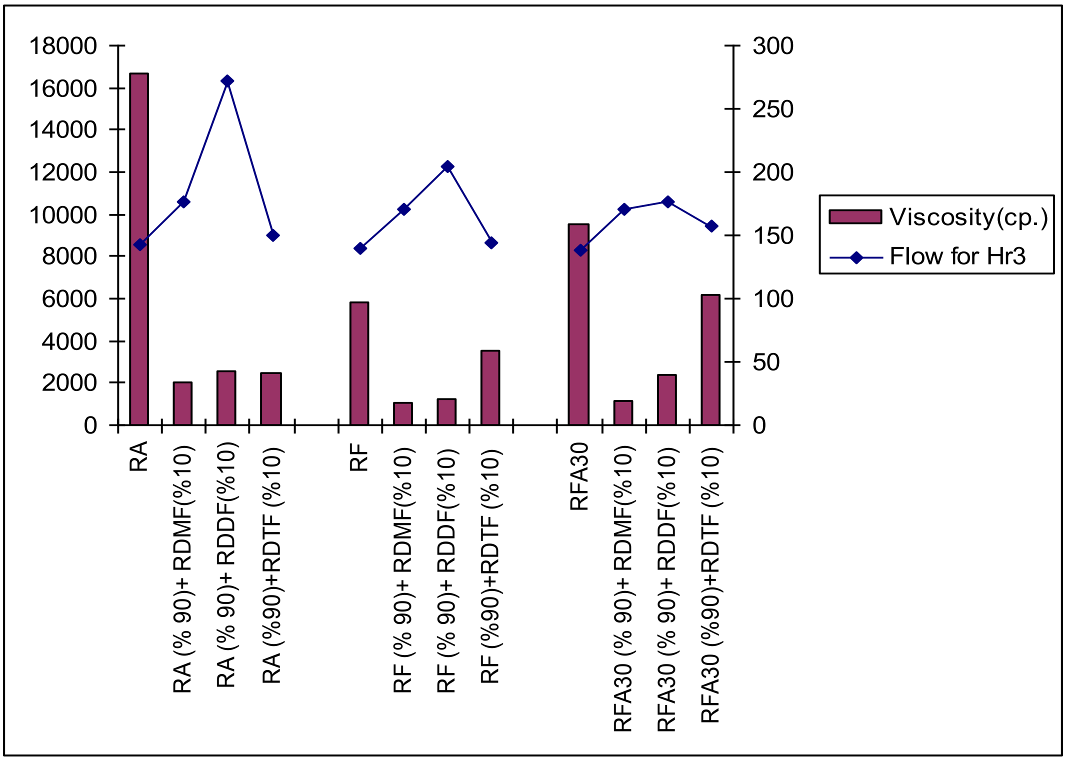


Figure 2: Viscosities of pure samples and flow table values of hardener 3 added versions of same mixes.

Flow of the material can also be examined with flow-ratio which can be calculated by flow area change with respect to the initial area (1).

$$\psi = \frac{A - A_0}{A_0} \tag{1}$$

Figure 3 shows the **v**iscosity and flow ratio relation of samples including hardener 6. The negative correlation between flow-ratio and viscosity can be seen.

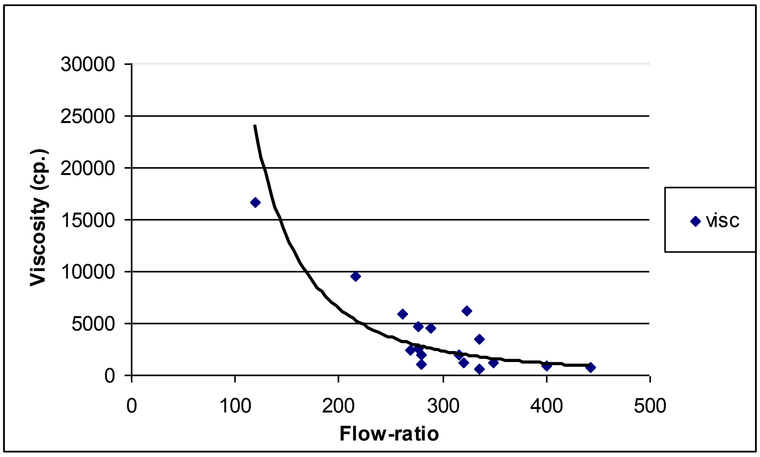


Figure 3: Viscosity and flow ratio relation of samples including hardener 6.

Pot-life tests were applied to a great number of samples. Even before the real experiments a lot of trials are done to reach optimum pot-life times and determine the optimum hardener quantity. For increasing the performance benzyl alcohol was added to Hr 4 and Hr 5 ,10% of activator addition was enough for Hr 5 while it did less effect on Hr 4. So the determined activator quantity for Hr 4 was 30%.

If pot-lives are compared according to hardener types, a sequence like below is seen;
Hr 3 < Hr 1< Hr 5 + 10 %Act.< Hr 6 < Hr 4 + 30 % Act.< Hr 2 <Hr 5 < Hr 4 .
As the reactive diluent rate increases, pot-life times were also increased. This result can be seen on figure 4.

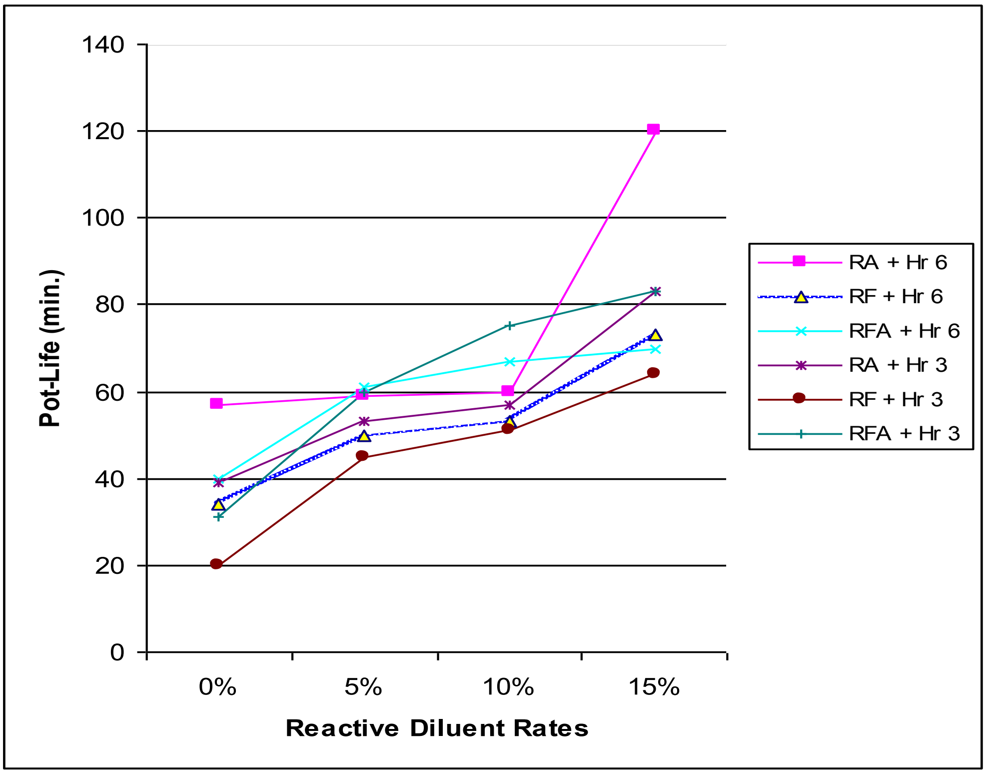


Figure 4: Pot-life comparison of different resin mixtures with addition of various rates of reactive diluents

For comparing reactive diluents, RDDF gave the shortest pot-lives while RDTF generally gave the longest pot-lives.

Bending and compression tests were applied to samples both for 1 day and 14 days. The applied load was 2kN for bending and 25kN for compression test. Hardeners performance sequence is below;

Hr 3 > Hr 4 > Hr 1 > Hr 2 > Hr 5+10% Act .> Hr 6 >Hr 5 > Hr 4+30% Act.

If the reactive diluents performances are compared, with mentioning that it may differ generally RDDF gave better results. Also the performance of RDTF was good but RDMF gave lower results.

Table 2 and 3 shows the 1 day and 14 days strength results of the samples. Results showed that for Hr 4, unactivated mixtures gave better results, but on the other hand activator addition increased the performance.

For comparing the resins, although the results are not very distinctive, RFA30 and RF resins showed generally better results than resin RA.

In the figure 5, 1 day bending test results of the hardener 3 and hardener 6 according to the reactive diluent compared. Its seen that the performance of hardener 3 is much better than hardener 6.

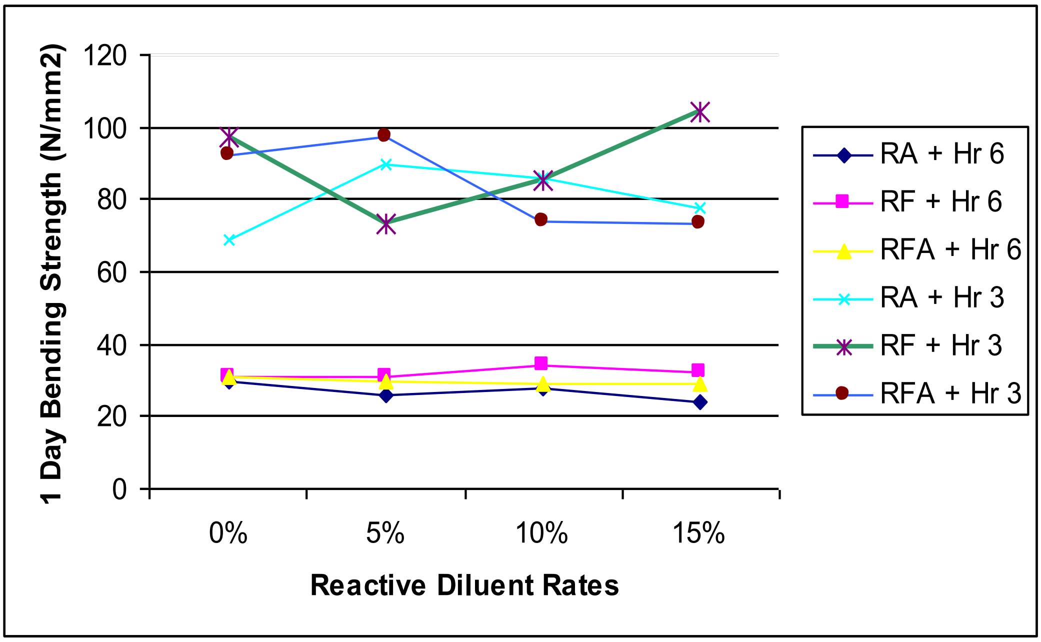


Figure 5: 1 day bending test results of resins with Hr 3 and Hr 6.

For the chemical resistance test, most effective solutions over epoxy were chosen, these are alcohol, 37 % formaldehyde, 15 % lactic acid and 20 % formic acid.

For a general evaluation, while the resistance of samples to formaldehyde and alcohol are good, most of them completed the 3 weeks of test time with no damage, but on the other hand no sample left undamaged towards the 15% lactic acid and 20% formic acid solutions. The level of the damage was changed according to the performances of samples. Chemical resistance test results are given on table 4.
The meanings of the letters used on table are ;

A- No damage
B- Low damage
C- Moderately damaged
D- Colour fading
E- Hardly damaged

Table 5.6: Bending and compressive strength results for 1 day samples

Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)	Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)
RFA30+HR 6	8,25	30,19	RFA30 + HR 3	24,59	83,73
RA+HR 6	7,9	41,59	RA + HR 3	18,53	75,94
RF+HR 6	8,32	40,46	RF + HR 3	25,95	79,74
RFA30 (% 90)+ RDMF(%10) +HR 6	7,75	32,25	RFA30 (% 90)+ RDMF(%10) +HR 3	19,64	46,38
RFA30 (% 90)+ RDDF(%10) +HR 6	8,43	39,6	RFA30 (% 90)+ RDDF(%10) +HR 3	26,95	89,18
RFA30 (%90)+RDTF (%10) +HR 6	8,17	42	RFA30 (%90)+RDTF (%10) +HR 3	25,96	71,75
RA (% 90)+ RDMF(%10) +HR 6	7,49	38,85	RA (% 90)+ RDMF(%10) +HR 3	22,9	59,99
RA (% 90)+ RDDF(%10)+ HR 6	8,31	41,65	RA (% 90)+ RDDF(%10) +HR 3	25,29	80,03
RA (%90)+RDTF (%10) + HR 6	6,67	40,26	RA (%90)+RDTF (%10) +HR 3	30,48	87,92
RF (% 90)+ RDMF(%10) +HR 6	9,12	45,37	RF (% 90)+ RDMF(%10) +HR 3	22,65	49,15
RF (% 90)+ RDDF(%10) + HR 6	9,22	44,1	RF (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RF (%90)+RDTF (%10) +HR 6	8,69	46,98	RF (%90)+RDTF (%10) +HR 3	27,64	71,64
RFA(%95)+RDMF (%5) +HR 6	7,93	37,41	RFA30 (%95)+RDMF (%5)+HR 3	25,96	80,89
RFA(%85)+ RDMF (%15) +HR6	7,8	38,5	RFA(%85)+ RDMF (%15) +HR 3	19,42	44,37
RA (%95)+RDMF (%5) + HR 6	7,01	35,47	RA (%95)+RDMF (%5) +HR 3	24,11	81,87
RA(%85)+RDMF (%15) +HR 6	6,49	37,48	RA(%85)+RDMF (%15) +HR 3	20,72	50
RF(%95)+RDMF (%5) +HR 6	8,37	41,1	RF(%95)+RDMF (%5) +HR 3	19,4	41,3
RF(%85)+RDMF (%15)+HR 6	8,52	39,66	RF(%85)+RDMF (%15) +HR 3	27,67	77,88
RA + HR 2	12,49	75,17	RA + HR 5	4,5	26,39
RA+RDMF (10%) + HR 2	22,06	63,84	RA+RDTF (10%) + HR 5	5,49	33,32
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	20,26	83,03	RA+RDMF (10%) +HR 5	5,32	28,13
RA + HR 1	10,05	40,10	RA +HR 5+ 10%Act.	7,81	44,2
RA+RDMF (10%) + HR 1	22,1	44,17	RA+RDMF(10%)+HR 5+10%Act.	19,22	53,07
RA +RDDF (10%)+ HR 1	24,97	56,63	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	20,11	46,06	RA+RDTF (10%)+HR 5+10%Act.	23,66	68,92
RA (100) +HR 4	22,25	39,63	RA (100)+ HR 4+ 30% Act.	6,12	10,43
RA+RDMF (10%)+HR 4	23,22	42,36	RA+RDMF (10%)+ HR 4+ 30% Act.	1,71	2,76
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	25,72	54,12	RA+RDTF (10%)+ HR 4+ 30% Act.	3,79	6,35

Note: The grey cells show two day strength results.

Table 5.7: Bending and compressive strength results for 14 day of samples

Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)	Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)
RFA30+HR 6	10,64	56,57	RFA30 + HR 3	26,38	97,00
RA+HR 6	6,4	41,24	RA + HR 3	26,71	97,21
RF+HR 6	10,83	58,55	RF + HR 3	26,89	93,08
RFA30 (% 90)+ RDMF(%10) +HR 6	12,96	68,6	RFA30 (% 90)+ RDMF(%10) +HR 3	23,69	78,18
RFA30 (% 90)+ RDDF(%10) +HR 6	13,32	67,57	RFA30 (% 90)+ RDDF(%10) +HR 3	30,69	103,73
RFA30 (%90)+RDTF (%10) +HR 6	9,71	51,54	RFA30 (%90)+RDTF (%10) +HR 3	29,33	90,87
RA (% 90)+ RDMF(%10) +HR 6	9.68	57,31	RA (% 90)+ RDMF(%10) +HR 3	23,33	62,74
RA (% 90)+ RDDF(%10)+ HR 6	8,82	43,69	RA (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RA (%90)+RDTF (%10) + HR 6	9,43	48,54	RA (%90)+RDTF (%10) +HR 3	28,04	98,34
RF (% 90)+ RDMF(%10) +HR 6	12,04	64,63	RF (% 90)+ RDMF(%10) +HR 3	20,99	58,76
RF (% 90)+ RDDF(%10) + HR 6	14,22	78,86	RF (% 90)+ RDDF(%10) +HR 3	29,14	95,24
RF (%90)+RDTF (%10) +HR 6	12,2	71,85	RF (%90)+RDTF (%10) +HR 3	27,82	76,42
RFA(%95)+RDMF (%5) +HR 6	10,68	52,53	RFA30 (%95)+RDMF (%5)+HR 3	23,76	71,99
RFA(%85)+ RDMF (%15) +HR6	12,72	60,15	RFA(%85)+ RDMF (%15) +HR 3	21,69	58,27
RA (%95)+RDMF (%5) + HR 6	9,3	47,87	RA (%95)+RDMF (%5) +HR 3	23,3	74,05
RA(%85)+RDMF (%15) +HR 6	12,24	63,87	RA(%85)+RDMF (%15) +HR 3	19,29	56,12
RF(%95)+RDMF (%5) +HR 6	14,91	73,18	RF(%95)+RDMF (%5) +HR 3	22,7	62,2
RF(%85)+RDMF (%15)+HR 6	19,78	80,77	RF(%85)+RDMF (%15) +HR 3	19,48	48,79
RA + HR 2	16,07	82,01	RA + HR 5	5,62	32,25
RA+RDMF (10%) + HR 2	18,08	58,16	RA+RDTF (10%) + HR 5	6,02	35,18
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	23,36	77,78	RA+RDMF (10%) +HR 5	6,18	30,69
RA + HR 1	17,77	43,46	RA +HR 5+ 10%Act.	9,58	45,62
RA+RDMF (10%) + HR 1	19,21	41,43	RA+RDMF(10%)+HR 5+10%Act.	10,35	47,26
RA +RDDF (10%)+ HR 1	24,97	56,93	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	22,04	47,21	RA+RDTF (10%)+HR 5+10%Act.	19,57	49,88
RA (100) +HR 4	24,17	53,68	RA (100)+ HR 4+ 30% Act.	5,36	7,54
RA+RDMF (10%)+HR 4	25,03	54,98	RA+RDMF (10%)+ HR 4+ 30% Act.	3,49	6,5
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	26,88	64,25	RA+RDTF (10%)+ HR 4+ 30% Act.	5,69	8,76

On the following table 4, chemical resistance test results were given.

Table 4: Results of chemical resistance test

No.	Chem.	1.week	2.week	3.week	1.week	2.week	3.week	Chem.	No.
1	Formald.	A	A	B	A	A	A	Formald.	9
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	E	E	C	C	C	Formic A	
	Lactic A	C	C	E	C	C	C	Lactic A	
2	Formald.	A	A	A	A	A	A	Formald.	10
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	E	E	C	C	E	Formic A	
	Lactic A	C	C	E	C	C	C	Lactic A	
3	Formald.	A	A	A	A	A	A	Formald.	11
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	B	C	C	C	E	E	Formic A	
	Lactic A	B	C	C	C	C	E	Lactic A	
4	Formald.	A	A	A	A	A	A	Formald.	12
	Alcohol	A	A	A	A	A	B	Alcohol	
	Formic A	A	C	C	E	E	E	Formic A	
	Lactic A	B	C	C	E	E	E	Lactic A	
5	Formald.	A	A	A	A	A	A	Formald.	13
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	C	C	C	C	C	Formic A	
	Lactic A	B	B	C	C	E	E	Lactic A	
6	Formald.	A	A	A	A	A	A	Formald.	14
	Alcohol	A	A	A	A	B	B	Alcohol	
	Formic A	E	E	E	C	E	E	Formic A	
	Lactic A	C	E	E	E	E	E	Lactic A	
7	Formald.	A	A	A	A	A	A	Formald.	15
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	A	B	B	C	E	E	Formic A	
	Lactic A	A	B	B	B	E	E	Lactic A	
8	Formald.	A	A	A	A	A	A	Formald.	R
	Alcohol	A	A	B	A	A	A	Alcohol	
	Formic A	E	E	E	B	C	C	Formic A	
	Lactic A	E	E	E	B	C	C	Lactic A	

Table shows that the performance of bisphenol A is much better than the one for bisphenol F and bisphenol A/F. Bisphenol F and bisphenol A/F has the same resistance nearly, they are damaged greatly by formic and lactic acid solutions, but bisphenol F is also unresistant to formaldehyde even its damage is very slight. It is the only mixture which was damaged by formaldehyde.

Hr.3 and Hr1 performs better, but the mixture with Hr.3 started to decaying 1 week later than the mixture with Hr.1 for lactic and formic acid solutions. Hr.2, also showed the same result with Hr1, The worst performance is the one for the mixture with Hr.5, there are samples which has same results with Hr.5 after 3 weeks time but it started decaying more quick than them. It was also damaged by alcohol unlike most of the samples. It was seen that performance increases with decreasing amount of reactive diluent. This was a parallel result with compressive and bending tests results.

The functionality of reactive diluents affect also performance, the mixture with RDTF performed best. The mixture with RDMF followed it but the one with RDDF performed worst.

The presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives . The resins cure with low shrinkage, so that the various surface contacts set up between the resin and adherent. Table 5 shows the pull-off test results.

Table 5: Pull-off test results showing the adhesion strength f_h values and fracture surface of the samples.

Sample	1. value (MPa)	2.value (MPa)	3. value (MPa)	f_h (MPa)
RF + Hr.3. + Sand	5,12	4,64	4,40	4,72
Fracture surface	A	-/Y	-/Y	
RFA30 + Hr.3.+ Sand	4,70	5,06	4,34	4,70
Fracture surface	-/Y	A	-/Y	
RA +Hr.3 + Sand	8,52	9,12	-	8,82
Fracture surface	A	A	A	
RA (%95) + RDMF (%5)+ Hr.3 + Sand	4,17	3,20	3,60	3,66
Fracture surface	-/Y	Y	Y	
RA (%90) + RDMF (%10)+ Hr.3 + Sand	3,42	2,17	2,45	2,68
Fracture surface	-/Y	Y	Y	
RA (%90) + RDDF (%10)+ Hr.3 + Sand	5,02	3,58	5,86	4,82
Fracture surface	-/Y	Y	A	
RA (%90) + RDTF (%10)+ Hr.3 + Sand	4,96	4,42	4,66	4,68
Fracture surface	-/Y	-/Y	-/Y	
RA (%85) + RDMF (%15)+ Hr.3 + Sand	2,78	3,74	3,56	3,36
Fracture surface	Y	-/Y	-/Y	
RA + Hr.1 + Sand	5,64	3,40	5,09	4,71
Fracture surface	A	-/Y	-/Y	
RA + Hr.2 + Sand	14,6	13,8	-	14,2
Fracture surface	A	A	A	
RA + Hr.4 + Sand	2,96	4,02	4,27	3,75
Fracture surface	-/Y	B	B	
RA +Hr.5 + Sand	2,02	1,96	3,64	2,54
Fracture surface	Y	Y	A/B	
RA + Hr.5 + % 10 Activator + Sand	10,16	8,76	-	9,46
Fracture surface	A	A	A	
RA (%90) + RDDF (%10)+ Hr.5 + Sand	5,80	4,22	3,24	4,42
Fracture surface	A	A/B	Y	
RA (%95) + RDTF (%5)+ Hr. 3 + Sand	6,70	5,45	3,45	5,20
Fracture surface	A	A/B	-/Y	

Performance sequence of hardeners are seen below;

Hr 2 >Hr 5+10% Activator > Hr 3 > Hr 1 > Hr 4 > Hr 5

Figure 6 shows the resin performances for hr 3 mixtures.

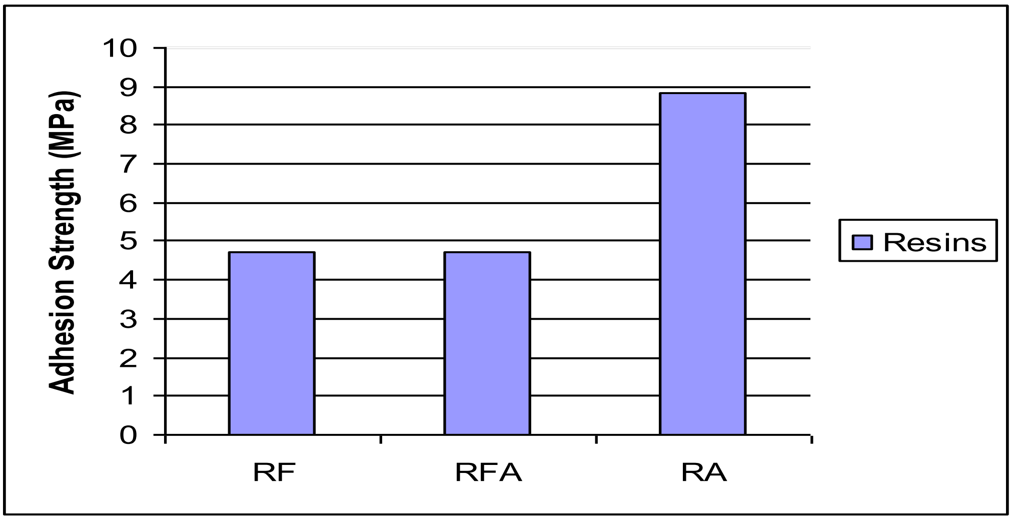


Figure 6 : Effect of diluent type on adhesion strength of resin A and hardener 3.

Reactive diluent addition lowered the results. For RDMF , the highest value was reached with the lowest reactive diluent ratio. But unexpectedly the results of 15% RDMF added sample performed slightly better then 10% of RDMF samples. Even 5% reactive diluent addition decreases the adhesion strength in huge amounts.

After completing this experiments, in the final part, the conclusions revealing from this study are given and the possible chemical reasons are discussed. The major result of this study is the great increase in mechanical strength caused by the epoxy resin and hardener usage in concrete. This study also confirmed the information about epoxy resins that is previously known.

1. INTRODUCTION

1.1 Epoxy

The term 'epoxy' refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms that are already bonded in some way. The simplest epoxy is a three-member ring structure known by the term 'alpha-epoxy' or '1,2-epoxy'. The idealised chemical structure is shown in the figure below and is the most easily identified characteristic of any more complex epoxy molecule [1]. In the figure 1.1. idealised chemical structure of a simple epoxy is seen.

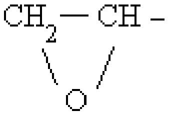


Figure 1.1: Idealised chemical structure of a simple epoxy (Ethylene Oxide) [1]

The non-epoxy part of the molecule may be aliphatic, cycloaliphatic or highly aromatic hydrocarbon or it may be non-hydrocarbon and possibly polar. It may contain unsaturation. Similar remarks also apply to the chain extension/cross-linked products of great diversity may be obtained [2].

Usually identifiable by their characteristic amber or brown colouring, epoxy resins have a number of useful properties. Both the liquid resin and the curing agents form low viscosity easily processed systems. Epoxy resins are easily and quickly cured at any temperature from 5°C to 150°C, depending on the choice of curing agent [1].

The molecular weight of epoxy resins affects the cross-linking. Aromatic structure in benzene rings gives high chemical resistance and strength. Among chemical bond ether, hydroxyl groups and all aromatic ring abundance provides adhesion property to epoxy. This and other properties are modified by the choice of hardener [3].

The large family of epoxy resins represent some of the highest performance resins of those available at this time [1]. These synthetic, thermal-setting resin having excellent adhesion to a wide variety of materials, good resistance to chemical attack and water penetration, outstanding electrical properties, low or moderate curing temperatures, low shrinkage on curing [4]. One of the most advantageous properties of epoxies is their low shrinkage during cure which minimises fabric 'print-through' and internal stresses. High adhesive strength and high mechanical properties are also enhanced by high electrical insulation and good chemical resistance. Good optical properties that is widely used in a variety of formulations for strain gage backings, adhesives, caulking compounds, casting compounds, sealants, varnishes and paints, laminating resins are for a variety of industrial applications [1]. These properties are used in such industries; civil engineering, epoxy composites, coil coatings, marine and protective coatings, photocure coatings, photo elastic adhesives, model materials, potting and encapsulation [5]. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in aircraft components. As a laminating resin their increased adhesive properties and resistance to water degradation make these resins ideal for use in applications such as boat building. epoxies are widely used as a primary construction material for high-performance boats or as a secondary application to sheath a hull or replace water-degraded polyester resins and gel coats [1].

The figure 1.2. below shows the idealised chemical structure of a typical epoxy of the ester[1]. There are no ester groups in this molecular chain.

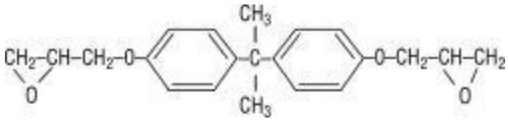


Figure 1.2: Idealised chemical structure of a typical epoxy of the ester[1].

Epoxies differ from polyester resins in that they are cured by a 'hardener' rather than a catalyst. The hardener, often an amine, is used to cure the epoxy by an 'addition reaction' where both materials take place in the chemical reaction. The chemistry of this reaction means that there are usually two epoxy sites binding to each amine site. This forms a complex three-dimensional molecular structure[5].

Since the amine molecules 'co-react' with the epoxy molecules in a fixed ratio, it is essential that the correct mix ratio is obtained between resin and hardener to ensure that a complete reaction takes place. If amine and epoxy are not mixed in the correct ratios, unreacted resin or hardener will remain within the matrix which will affect the final properties after cure. To assist with the accurate mixing of the resin and hardener, manufacturers usually formulate the components to give a simple mix ratio which is easily achieved by measuring out by weight or volume [1].

1.2. History of the Epoxy Resin

Although the first products that would now be called epoxy resins were synthesized early as 1891, it was now not until the independent work of Pierre Castan in Switzerland and Sylvan Greenlee in the United States that commercial epoxy resins were marketed in the 1940’s, although similar resins had been patented in the 1930’s. The earliest epoxy resins marketed were the reaction products of bisphenol A and epichlorohydrin and this is still the major route for the manufacture of most of the resins marketed today, although there are many other types of resins available[7].

In 1936 Castan produced a bisphenol-A based epoxy resin via reaction with epichlorohydrin and subsequently prepared a thermoset composition after reaction of the resin with phtalitic anhydride. The use of the hardened resin as foreseen in dental products but initial attempts to market the resin were unsuccessful. The patents were licensed to CIBA AG of Basel, Switzerland and in 1946, the first epoxy adhesive was shown at the Swiss Industries Fair. During 1939 Sylvan Greenlee produced a high molecular weight resin from bisphenol-A and epichlorohydrin which was subsequently esterified with unsaturated fatty acids to provide an air-drying coating. His first patent issued in 1948 [8].

Pierre Castan investigated potential resins which could be readily moulded at low pressures for the replacement of vulcanite as a denture base material. The BPA-epoxy resins could be cured by reaction of epoxy groups with phtalitic anhydride without the evolution of low molecular species and hence did not require high moulding pressures. An alternative acrylic resin is now used for denture base. Epoxy adhesives and casting resins were marketed in the USA in 1946.

Greenlee produced resins which were similar to those of Castan but with a somewhat higher molecular weight with the objective of developing superior surface coatings.

The epoxy coatings developed by Greenlee offered improved adhesion, hardness, inertness and thermal resistance compared with alkyd or phenolic resins, following the first patent application [7].

Immediately after World War II, Greenlee and co-workers patented for DeVoe and Raynolds a series of epoxy resin compositions encompassing resins and resin esters. Meanwhile, further developed epoxy resins for casting, laminating and adhesive applications [8].

1.3 Recent Developments in Epoxy Resins

A number of recent developments in epoxy resins have been the result of modifications of epoxy resins.

An important example is the preparation of a water dispersible product by graft polymerization of, for example ,styrene-methacrylic acid copolymer onto an aliphatic backbone of a high-molecular weight epoxy resin.

The acrylic modified epoxy copolymer can be neutralized via the pendant carboxyl groups to provide a water-dispersible system with good hydrolytic stability. The grafting is presumed to occur onto the methylene hydrogens of the glycidyl group in the epoxy resin.

The product is a mixture of ungrafted epoxy resin as well as acrylic copolymer with pendant carboxyl groups and cure is effected via amino-formaldehyde resins to produce coatings for beer and beverage cans.

Another example of modified epoxy resin is the area of cathodic electrodepositation whereby a low molecular weight epoxy resin is reacted via the epoxy terminal groups with a primary or secondary amine to form an adduct which is solubilized with an acid [8].

1.4 Chemical Structure

Epoxies consist of two components that react with each other forming a hard, inert material. Part A consists of an epoxy resin and Part B is the epoxy curing agent, sometimes called hardener[8]. Many of the commercial liquid resins consist essentially of the low molecular weight diglycidyl ether together with small quantities of higher molecular weight polymers.

The epoxy resins of the glycidyl ether type are usually characterized by six parameters ;

- Resin viscosity (for liquid resins)
- Epoxy equivalent
- Hydroxyl equivalent
- Average molecular weight (and molecular weight distribution
- Melting point (of solid resins)
- Heat distortion temperature (deflection temperature under load) of cured resin [2].

Any multifunctional, f ≥2, phenolic compound is a potential starting material for the manufacture of epoxy resins. Although many have been studied, only a few have any commercial significance and these are ‘formulated’ to meet specific requirements . Also some monofunctional phenols have been reacted with epichlorohydrin to produce monofunctional reactants for use as modifying diluent agents [7].

Some bisphenol resins used as Part A ,such as bisphenol A, bisphenol F or Epoxy-Novolac resins. But generally used Part A epoxy resin is Bisphenol A .Bisphenol-A (BPA) is an white, organic compound composed of two phenol rings connected by a methyl bridge, with two methyl functional groups attached to the bridge. The hydroxy functional group on each phenol is *para-* to the connecting methyl bridge. A general synthesis for making BPA is a condensation reaction of acetone and phenol together with hydrochloric acid, which acts as a catalyst. This is a very exothermic reaction, with an enthalpy value of –368 kJ/mol. As a result, it is assumed that extensive cooling is required during BPA production [8].

Bisphenol A is used as an intermediate in the manufacture of epoxy, polycarbonate, phenoxy, polysulfone and certain polyester resins. It is also used in flame retardants and rubber chemicals, and as a fungicide [9]. One type of epoxy is the product of the reaction between epichlorohydrin and BPA. In the figure 1.3. catalyst of Bisphenol A is seen. These epoxies are used as food-contact surface coatings for cans, metal jar lids, coatings and finishes, automobile parts, adhesives, aerospace applications, and as a coating for PVC water pipe walls. Polycarbonate plastics are used with CD and CD-ROM manufacturing, in automotive parts, high-impact windows, household appliances, food packaging, and plastic bottles for water and baby milk. Some of the polymer forms are used as dental sealants and bonding agents [10].

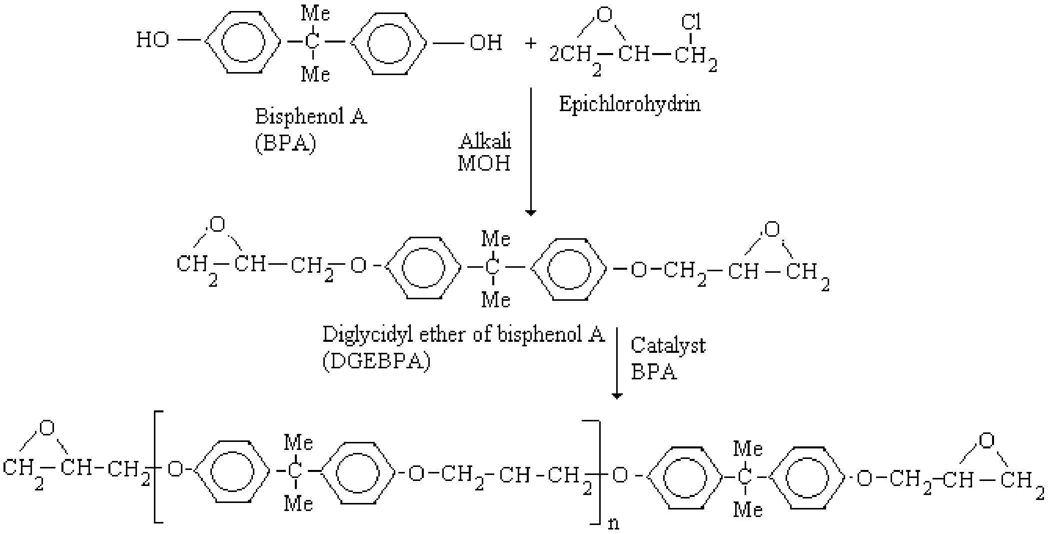


Figure 1.3: Catalyst of Bisphenol A [7]

Bisphenol A – epoxy resins could be cured by reaction of epoxy groups with phtalitic anhydride without the evolution of low molecular species and did not require high molding pressure [7].

Epoxy resin begins with the reaction of two compounds, as it is said above, generally used resin bisphenol A - Bis A and epichlorohydrin [11].

Other raw material of epoxy is epichlorohydrin. Epichlorohydrin is used to put the resin products in an order. In the figure 1.4. formation of epichlorohydrin is seen. Because, the epoxy group reacts in readily because of the existence of alkaly catalizors and then the new epoxy chain is put in order by dehydrochlorination. In the figure 1.5. low molecular weight prepolymer which is containing reactive epoxy groups is seen.

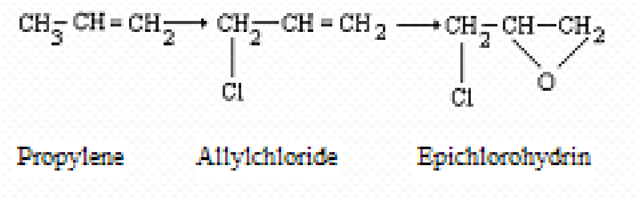


Figure 1.4: Formaton of epichlorohydrin [7]

More epichlorohydrin is used to close chain ends with epoxy groups. At first low molecular weight prepolymer which is containing reactive epoxy groups is formed.

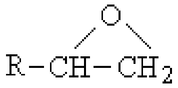


Figure 1.5: Low molecular weight prepolymer which is containig reactive epoxy groups [3]

Nearly 70% of all epichlorohydrin is used in the production of epoxy resin. This colourless liquid with its irritating chloroform like odor finds it way into the production process of various synthetic materials.

The reaction between bisphenol A and epichlorohydrin removes unreacted phenol and acetone and attaches two glycidyl groups to the ends of the bisphenol A, creating a 'diglycidyl ether of bisphenol A (called DGEBA)', which is standard epoxy resin. The glycidyl group on both ends of the bisphenol A are also referred to as an oxirane or ‘epoxy group'. The size of the resulting molecule (and hence its molecular weight) depends upon the ratio of epichlorohydrin to bisphenol A [13].

By the ratio of epichlorohydrin/ bisphenol A, molecular weight is controlled. If this ratio is low, high molecular weight is obtained and a solid product is formed. If this ratio is high, liquid products are formed. Liquid epoxy resins are based on generally bisphenol f [3].

The repeat unit (n) size in prepolymer is important for polymer properties. Polymer is viscous liquid at small n values. When the repeat unit (n) number reaches nearly 25, polymer becomes hard plastic at room temperature [12].

Bisphenol F is another common epoxy resin. The dihydric phenol which is produced by reaction of phenol with formaldehyde is called “Bisphenol F” [7]. In figure 1.6. chemical structure of bisphenol F is seen.

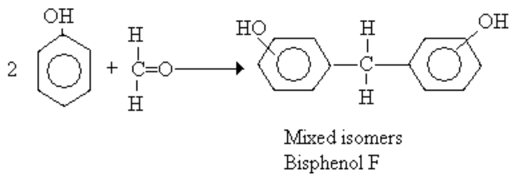


Figure 1.6: Chemical structure of bisphenol F [7]

Bisphenol F is more active than the Bisphenol A and it has lower viscosity, so that it costs more than it. When these two resins are used together, the crystallization probability is decreased. For this reason generally the mix of these resins are used. The mixture can be done stoichiometrically or with some other proportions[7] .

Bisphenol F resins doesn’t have much applications. Glycol diepoxide resins also are epoxy functional resins and are formed by the reaction of polyglycol and epichlorohydrin[3] .

Resins can be manufactured from Bisphenol F by similar methods to those used for Bisphenol A and epichlorohydrin with a catalyst such as NaOH. These resins have lower viscosities than the equivalent DGEBA [7].

Epoxy-novolac resins are also useful resins which are preferred especially because of their excellent temperature and chemical resistance [11]. They are formed by the reaction of formaldehyde and fenole. Although they have many superior properties[3]. The simples novolac could be considered to be bisphenol F with novolacs, ranging upward in molecular weight from this to containing 10 to 12 phenolic hydroxyls [14]. When cured with room temperature these resins have similar thermal stability to ordinary bisphenol A epoxies. However when they are cured with high-temperature hardeners such as methyl “nadic” anhydride both thermal degradation stability and heat deflection temperatures are considerably improved [2]. Novolac resins have some disadvantages; their difficult production process and system may become brittle because of high degree of cross-linking and their high viscosity limits their usage [3]. In the figure 1.7. structure of epoxy-novolac resin is seen.

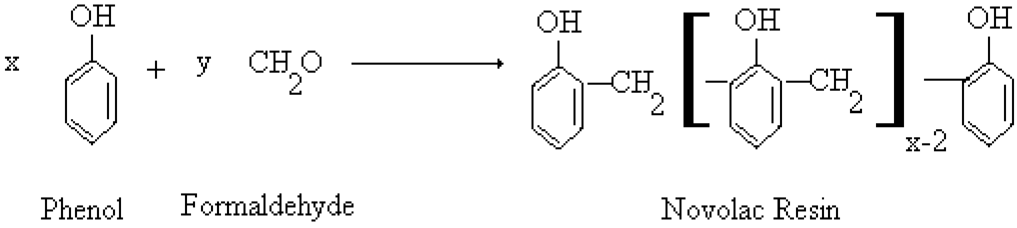


Figure 1.7: Epoxy-Novolac resins [3]

In order to convert epoxy resins to hard, infusible thermoset networks, a cure process with a hardener (or curing agents) is needed. In figure 1.8. the scheme for cure of epoxy resin is seen. The cure of epoxy resins involves the formation of a rigid three-dimensional network by reaction with hardeners which have more than two reactive functional groups, that is, functionality is $f > 2$. Often $f \geq 4$ for common hardeners for BPA resins which often have an effective functionality of two, but may be higher when the cure temperature is high enough for the secondary hydroxyl groups to react. In figure 1.9. the curing mechanism of an amine type hardener is seen. Equation 1.1. is for calculating the extent of reaction.

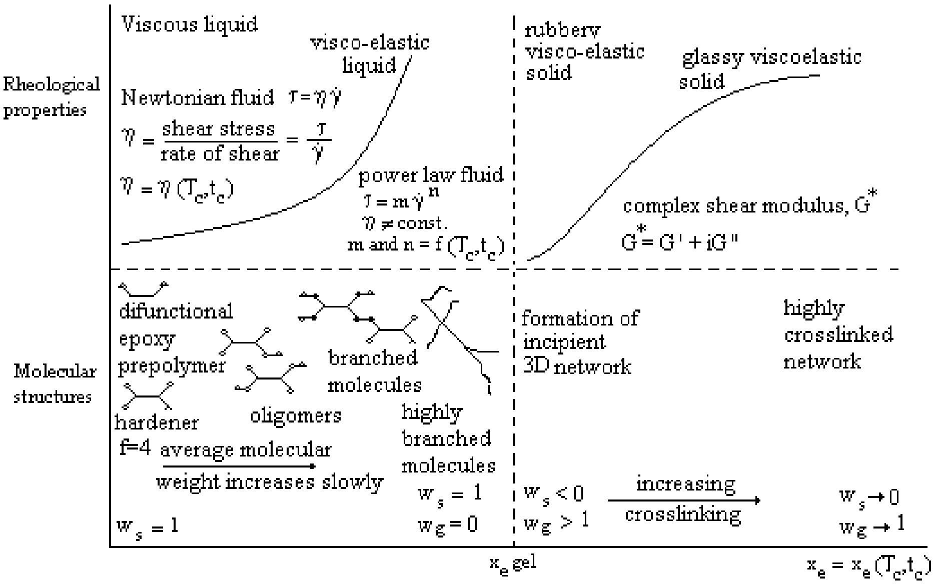


Figure 1.8: The scheme for cure of epoxy resins [7]

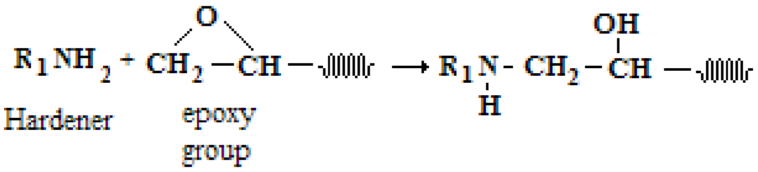


Figure 1.9.: Curing mechanism of an amine type hardener [15]

The extent of reaction;

$$X_e = \frac{E_0 - E(t_c)}{E_0} \quad (1.1)$$

where E_0 is the initial concentration of epoxy groups and E (t_c) is their concentration at cure time tc. Tc is the cure temperature. Equation 1.2. and 1.3. are given for calculating the sol and gel fraction.

$$\text{The sol fraction } w_s = \frac{\text{weight of soluble molecules}}{\text{total weight of the sample}} \quad (1.2)$$

$$\text{The gel fraction } w_{gel} = \frac{\text{weight of cross-linked network, gel}}{\text{total weight of the sample}} \quad (1.3)$$

Except gelation, the cure process is continuous. Initially there is reaction between epoxy and hardener reactive groups so that somewhat larger molecules are formed. As cure proceeds, larger and larger molecules are formed but it should be noted that the average molecular size is still small even when half the reactive groups have reacted. When the molecular size increases as cure progresses, some very highly branched molecules are formed and then more and more highly branched structures developed. The critical point is gelation when the branched structures extend throughout the whole sample. Before the gelation the sample is soluble in suitable solvents but after the gel point the network will not dissolve but swells as it absorbs solvent. At the gel point small and branched molecules are present which are soluble, hence the curing sample contains sol as well as gel fractions. The gel initially formed is weak and can be easily disrupted. To produce a structural material, cure has to continue until most of the sample is connected into the three-dimensional network so that the sol fraction becomes small and for many cured products it has to be essentially zero.

When the prepolymer and diamine (curing agent) is mixed, cross-linking occurs between epoxy groups[7]. Figure 1.10. shows the cross-linking of epoxy prepolymer. Cross-linking of epoxy resins can also be done by using polyanhydrides. In figure 1.11 it shows this conditions, cross-linking proceeds with –OH groups in epoxy chains[16]. Figure 1.11 shows the cross-linking of prepolymer by using polyanhydrides.

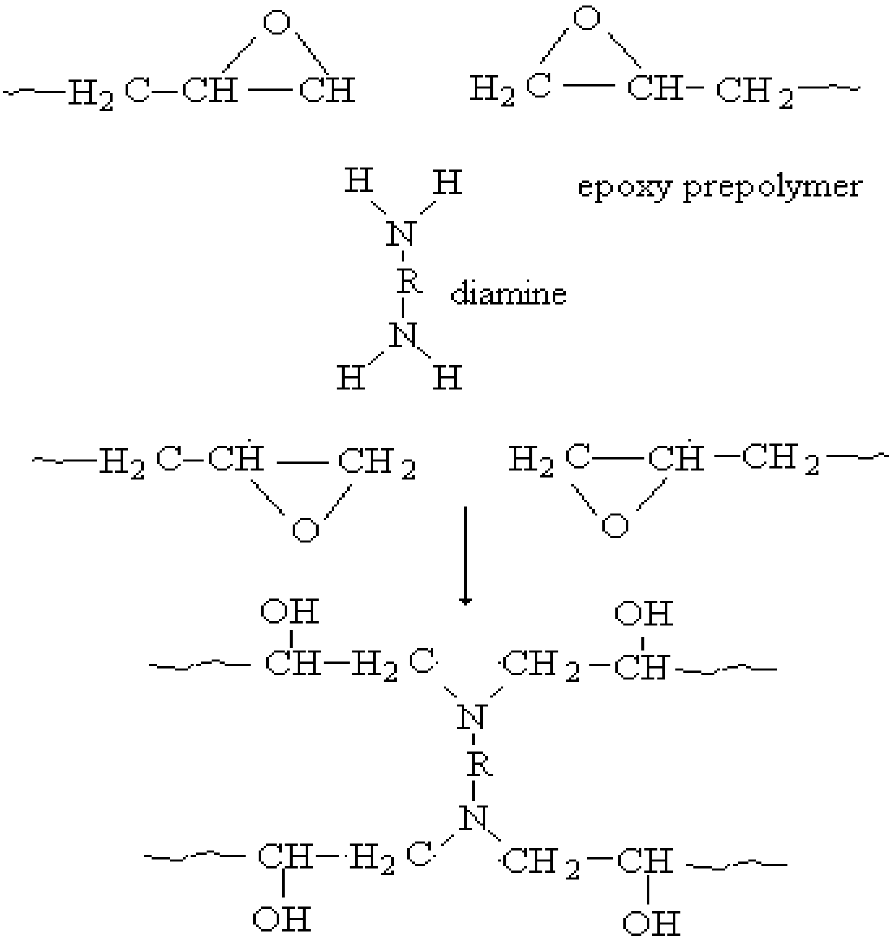
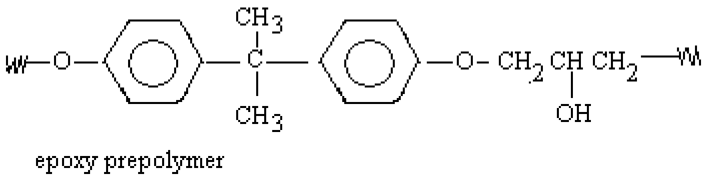


Figure 1.10: Cross-linking of epoxy prepolymer [16]



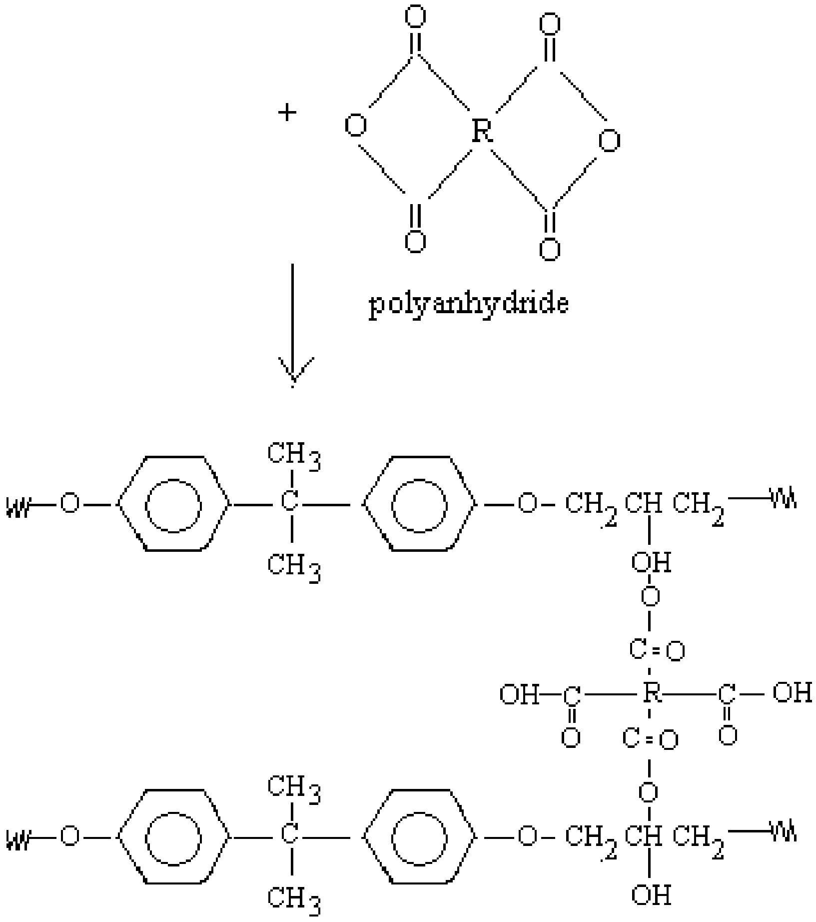


Figure 1.11: Cross-linking of prepolymer by using polyanhydrides [16]

As cure proceeds there are major changes in the properties of the epoxy resins. Initially the resin- hardener mixture is fluid and finally an elastic solid is produced. The glass-transition temperature of the curing resin increases as cure proceeds. For cure temperatures well above T_g, the rate of reaction between the epoxy and hardener reactive groups is chemically kinetically controlled. When $\Delta T = T_c - T_g$ becomes small the curing reactions become diffusion controlled, and will eventually become very slow and finally will stop. For products for which it is necessary to ensure complete reaction of all epoxy groups it is a normal practice to post-cure the resin at an elevated temperature. For successful application of epoxy resins it is necessary to select a suitable hardener and then cure the resin to attain a controlled network structure[7].

The ‘amine' curing agent has a molecular structure which typically consists of four hydrogen ‘arms and legs'. These hydrogens react with the oxirane (epoxy group) ring unit on the ends of the epoxy resin. The result is a new carbon-hydrogen bond, this time using the hydrogen from the curing agent and freeing the epoxy group's hydrogen to unit with the group's oxygen to form an OH (hydroxyl) pendant. This hydroxyl group contributes to the epoxy's outstanding adhesion to may substrates. The aromatic ring unit, which the hydroxyls attach to, helps provide the epoxies positive thermal and corrosion properties.

Because there are at least four hydrogens on the curing agent they can react with four epoxy resin groups, which causes giant interlocking structures (in a process known as ‘cross-linking’) [12].

2. ADDITIVES FOR EPOXY RESINS

For a number of purposes the unmodified epoxy resin may be considered to have certain disadvantages. These disadvantages include high viscosity, high cost and too great a rigidity for specific applications [2].In addition to two main ingredients of an epoxy formulation, resin and curing agent, numerous other materials are available and have frequently been used to modify the properties and characteristics of epoxies, both uncured and in their cured form[7]. The resins are therefore often modified by incorporation of diluents, fillers, and flexibilisers and sometimes with other resins[2].

2.1 Diluents

Diluents are usually used as viscosity reducers in order to aid general processability as well as allowing for greater incorporation of other formulatory ingredients such as fillers and as a means of improving characteristics such as wetting and the incorporation of resins into various fibrous reinforcements.

In addition to viscosity, it is important to recognise that other properties will also be modified, the modified properties and the magnitude of this modification will depend on both the type and quantity of diluent used. In addition many of the materials capable of showing diluent effects has adverse toxicological characteristics, in many cases being more severe than those found with both resin and curative. Great care should therefore be taken in both selection and use.

Diluents can be classified as non-reactive and reactive diluents.

2.2 Non-reactive diluents

Non- reactive diluents are used to reduce viscosity in epoxy formulations. These include aromatic hydrocarbons such as toluene or xylene which are capable of reducing viscosity in a simple diglycidylether of bisphenol A (DGEBA) resin system sufficient to permit a room temperature viscosity approximately 20% of its initial value with a diluent loading about 5%. When used in this level, studies have shown that the level of impact on physical and mechanical properties are not usually dramatic, indeed in some cases the presence of the diluent has been shown to increase the extent of cure in the formulation, presumably through the reduction in viscosity providing a reaction medium more conducive to molecular mobility and thus reactivity. At higher concentrations however, the properties of the cured epoxy can deteriorate markedly and, due to their non-reactivity, diluents of this type can lead to the presence of voids in the cured polymer, primarily if the formulation is subjected to elevated temperature cure sufficient to allow vaporisation of the diluent [7]. This type of diluents has better flexibility an thermal mechanical shock resistance with addition of impact resistance when compared with reactive epoxy binders [3].

Other non-reactive materials which have been considered as potential diluents include dibutyl phthalate, styrene and various phenolic compounds.

In addition to the drawbacks mentioned above, since the compounds are not chemically bound into the cross-linked network, cured formulations containing these materials usually exhibit inferior chemical resistance [7].

2.3 Reactive diluents

Attempts at viscosity reduction with epoxies have generally made use of materials capable of chemical reaction with the epoxy resin, these generally referred to as reactive diluents [7]. They are active at the final and their efficiency is very small at the end of the cure [3].

Two major classes of reactive diluent can and have been utilised commercially, these being either epoxy-containing diluents or compounds which derive their reactivity from functional groups other than epoxide.

2.4 Epoxy-based reactive diluents

Two types of diluent can be considered under this classification; (i) mono-epoxy compounds and (ii) di/polyfunctional epoxies. With both classes the presence of the epoxide group(s) allows the diluent to participate, with the resin and curing agent, in the polymerisation and cross-linking reaction thus permitting the diluent to become chemically bound into the cross-linked network. Thus, to a degree, the use of reactive diluents can alleviate some of the performance reducing effects found with the non-reactive compounds.

Some mono epoxy reactive diluents which have been considered and indeed in some cases used to modify epoxy resin viscosity. Although capable of exerting a substantial viscosity-reducing effect, these materials essentially reduce the functionality of the reaction system leading to a decrease in the cross-link density of the cured formulation. Consequently important physical and mechanical properties and frequently affected, particularly the ability to exert a “high temperature capability”.

The extent to which both cured properties and initial viscosity are reduced will be a function of both diluent type and concentration. Thus choice of both parameters will clearly be crucial in order to derive the greatest reduction of viscosity with minimal cost to other properties.

In an attempt to preserve physical/mechanical properties at elevated temperatures, the use of polyfunctional epoxy diluents has been considered. Although to a degree they can be regarded as epoxy resins in their own right, their use in more conventional formulations, like those using a DGEBA as the basic resin component, has demonstrated their ability to provide viscosity reduction. Typical of the polyfunctional epoxy compounds which have been suggested as reactive diluents. In most cases, since the functionality of the system as a whole is not greatly affected by the incorporation of these materials, cross-link density, and therefore properties associated with it are not usually affected detrimentally. Indeed some property enhancement has been shown to be possible [7].

2.5 Non-epoxy based reactive diluents

Although epoxide-based reactive diluents are used in the majority of cases where viscosity reduction is considered desirable, a number of compounds which derive reactivity via non-epoxide groups have been considered. Most notable amongst these have been triphenyl phosphite and lactone compounds such as butyrolactone. Both materials have been shown to have effective viscosity-reducing characteristics, although frequently at the expense of an elevated temperature capability [7].

2.6 Fillers

Apart from the resin and curative, fillers are possibly the most common formulatory ingredient employed in the majority of epoxy formulations [7]. Fillers are used in tooling and casting application[2]. Literally hundreds of different types can and have been used to modify, in one form or another, the properties and characteristics of epoxies [7]. Not only do they reduce cost but in diluting the resin content they also reduce curing shrinkage, lower the coefficient of expansion, reduce exotherms and may increase thermal conductivity. Sand is frequently used in inner cores whereas metal powders and metal oxide fillers are used in surface layers. Wire wool and asbestos are sometimes used to improve impact strength [2]. Although fillers can be considered beneficial for many applications, disadvantageous characteristics such as increased density (and hence weight) together with an increase in viscosity which is likely to influence the processing behaviour of the formulation, obviously require serious consideration [7]. On the table 2.1. advantages and disadvantages of fillers are seen.

Table 2.1: Advantages and disadvantages of filler incorporation [7]

Advantages	Disadvantages
Reduced formulation cost Reduced shrinkage Improved toughness Improved abrasion resistance Reduced water absorption Increased heat deflection temperature Decreased exotherm Increased thermal conductivity Reduced thermal expansion coefficient	Increased weight Increased viscosity Machining difficulties Increased dielectric constant

2.7 Flexibilisers

In order to increase flexibility, and usually, in consequence, the toughness of the resin, plasticisers and flexibilisers may be added [2]. It is here that the distinction is usually made between plasticising and flexibilising materials, plasticisers acting in a non-reactive manner whilst flexibilisers is the term usually applied to materials that react with the epoxy system during cure [7]. Non-reactive plasticisers such as the conventional phthalates and phosphates have proved unsuccessful. Monofunctional materials, which in some cases also act as reactive diluents, have been used but are not of great importance.

More interest has been shown in polymeric flexibilisers, particularly the low molecular weight polyamides form dimer acid, the low molecular weight polysulphides, polyamines and the polyglycol diepoxides.

Using flexibilisers in addition to the usual amount of hardener, very flexible products may be obtained. Although in many respects they are similar to the liquid polysulphides, the amine flexibilisers differ in three important respects ;

- They reduce the reactivity of the system rather than increase it.
- They are compatible with a different range of room temperature hardeners.
- They have a lo level of odour [2].

2.8 Curing agents

To convert epoxy resins to hard thermoset network it is necessary to use cross-linking agents [7] . The chemical chosen to react with epoxides is referred to as the curing agent (or hardener), and it typically has active hydrogen attached to nitrogen, oxygen, or sulphur [1]. So curing agents are classified as nitrogen-containing, oxygen-containing, sulphur- containing and the others.

Curing can occur by either ;

(i) homopolymerisation initiated by a catalytic curing agent

(ii) polyaddition/copolymerisation reaction with a multifunctional curing agent

Mostly known curing agents are simple amines, acid anhydrides, phenol - formaldehyde and amino-formaldehyde resins. But nova days also polyfunctional amines, polybasic carboxylic acids, mercaptans and even inorganic chemicals are started to used as curing agents. Also some modifications can be made to these chemicals to gain preferred properties.

Choice of curing agent type can affect the properties of an epoxy resin when cured. As it is unusual for a single catalyst or curing agent to provide optimum characteristics in any given application, the identification and selection of a satisfactory curing agent is often, so it is a complex procedure [7]. The selection of the curing agent depends on many parameters and will determine, to a large extent, the performance of the final epoxy thermoset. The following points has to be considered ;

- Definition and mode of action of epoxy resin curing agents
- Parameters to consider for your selection in composite applications
- Description with key attributes of commercially available curing agents for composite applications [1]

2.8.1 Nitrogen-containing Curing Agents

The main groups included in nitrogen-containing curing agents are aliphatic amines, cycloaliphatic polyamines, aromatic polyamines, aromatic polyamines and their derivatives, catalysts and co-curing agents, hydrazine and hydrazides [7].

Aliphatic amine curing agents provide room temperature cure and short work lives at room temperature. Aliphatic amines are the most common curing agents used in the industry today [16].Most prominent aliphatic amines are ethyleneamines (such as TETA and TEPA), polyamides, polyamidoamines and imidazolines, mannich bases and association salts, ketimines and acrylonitrile adducts, propylenamines, fatty amines, polyetheramines, polymeric amines, araliphatic amines, dicyandiamide and biguanide derivatives[7]. Polyamide and amidoamine curing agents are a widespread kind of hardeners for epoxy resin systems are best described as toughened amines. These reaction products of aliphatic amines and mono or dimerized fatty acids are usually high in viscosity, amber in colour and provide a relatively slow cure response when used with an epoxy resin system[16]. On table 2.2. estimated usage quantities of curing agents are seen.

Cycloaliphatic polyamines are elevated temperature curing agents which are only used when the application requires better high temperature and/or chemical resistance. A relatively exacting mix ratio of epoxy resin to hardener is required in order to maximize performance [16].Also the cycloaliphatic polyamines and derivatives are a crowded class of nitrogen-containing curing agents which includes authentic cycloaliphatic polyamines, accelerated cycloaliphatic polyamines, adducts and mannich bases.

Table 2.2: Estimated world market for curing agents by type [7]

Hardener type	Weight (mmlb)	Relative use (%)
Amines -aliphatics	45	10
-cycloaliphatics	30	7
-aromatics	15	3
-dicyandiamide	10	2
Polyamides	5	16
Polyamidoamines	30	7
Phenol and amino formaldehyde resins	75	16
Carboxylic acid functional polyesters	100	22
Anhydrides	5	12
Polysulphides and polymercaptans	15	3
Catalysts	10	2
Total	50	100

Aromatic polyamines and derivatives are less basic than aliphatic or cycloaliphatic polyamines and react only slowly with epoxy resin. Typically they exhibit long pot-lives and require long periods at elevated temperature to attain optimum properties, they are divided into two branches; heat cured aromatic amines and room temperature cured aromatic amines.

Also tertiary amines, imidazoles and ureas are counted in catalysts and co-curing agents group. Imidazoles are curing agents for epoxy resins systems are usually used only when a production process demands a long work-life, a fast elevated temperature cure and good high temperature properties [7].

2.8.2 Oxygen-containing Curing Agents

Main branches of oxygen-containing curing agents are carboxylic acids and anhydrides, phenol formaldehyde resins and amino formaldehyde resins.

Carboxylic acids and anhydrides are the second most important family curing agents for epoxy resins. Although the acids are only practical in heat-cured surface coatings, or stoving enamels, they are nonetheless the most widely used epoxy curing agent type. Anhydrides are suited to most other heat cure applications.

Phenol formaldehyde resins can be reacted with formaldehyde to give resinous products, Phenol-Formaldehyde (P-F) resins, with a wide variety of commercial applications; it is been recorded that certain types being suitable as cross-linking agents for epoxy resins. Phenol novolac resins and resole resins are in this family of curing agents.

2.8.3 Sulphur-containing Curing Agents

The thiol or mercaptan group (-SH) is able to react with epoxy resin in an addition reaction. This requires catalysis at room temperature by amines which promote production of reactive mercaptide ions.

With mercaptan terminal polysulphides, whose functionality (typically 2) is too low for efficient cross-linking of di-functional bisphenol A epoxy resin, primary amines are used as initiators/co-curing agents. With polymercaptans where the functionality (typically 3) is adequate for efficient cross-linking, strongly basic tertiary-amines are used as initiators and rapid cure times result. Polysulphides and polymercaptans are included in sulphur- containing curing agents [7]. On table 2.3. advantages and disadvantages of most common curing agent types are seen.

Also amine-boron trihalide complexes, quaternary phosphonium salts and cationic salts are some of miscellaneous curing agent types [7].

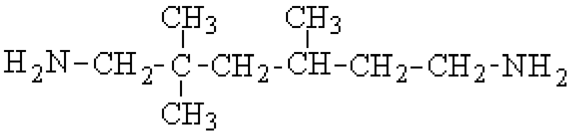
Table 2.3: Beneficial and negative properties of most common curing agent types [17]

Group of curing agent	Benefits	Negatives
ALIPHATIC AMINES	Room temperature cure Usually low viscosity Fast elevated temperature cure Low toxicity Provides good adhesion	Short work life Moderate high temperature performance - Poor bond strength above 80°C Poor chemical resistance Exothermic
AROMATIC & CYCLOALIPHATIC AMINES	Good high temp. properties Good chemical resistance Long work-life at room temperature	Must be heat cured Aromatic amines are biologically aggressive Requires precise mix ratio
IMIDAZOLES	Mixed work-life at room temperature of 1-2 day Very fast elevated temperature cure Excellent high temp stability and chemical resistance Good adhesion to most metals Forgiving mix ratio with epoxy resin Colour change helpful for complete cure determination	Requires heat cure Can only cure in small masses Relatively brittle polymer with poor T-Peel strength Imidazole curing agents are relatively expensive
ONE PART CURING AGENTS	No mixing required Usually has good high temperature properties Good metal adhesive	Must be heat cured Exothermic (Usually used in small masses) Cost
POLYAMIDS & AMIDOAMINES	Great general purpose adhesives that bond well to most substrates Long work-life at room temperature Non-critical mix ratios Very low toxicity, FDA acceptable for food contact Non-corrosive, Non-DOT regulated, Worker-safe products	Very slow to room temperature cure. Typical requirements 2-7 days at room temperature or 1-2 hours at 65°C.

2.9. Curing Agents Used in This Study

2.9.1 2,2,4- 2,4,4 Trimethyl-hexamethylene Diamine (TMD) (Hardener 1)

TMD (Trimethylhexane diamine) was developed for use as a urethane intermediate is actually an equal part mixture of the 2,2,4- and 2,4,4-trimethyl hexamethylene diamine isomers. On figure 2.1. chemical structure of TMD is seen.



$$H_2N-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-NH_2$$

Figure 2.1: 2,2,4- 2,4,4 Trimethyl-hexamethylene Diamine (TMD) [18]

Their physical characteristics derived from their low molecular weights ; low viscosity, corrosivity, irritancy to the eyes and skin. They are high in reactivity and have a strong tendency to carbonate due to unhindered primary aliphatic amine functionality. They also have an ability to give moderate film flexibilities due to the moderate chain distances between the cross-link sites. Additionally, their high hydrocarbon contents make them hydrophobic and, problematically, only moderately compatible with epoxy resins.

Adduction with epoxy resin, mannich base formation or salting with acidic accelerators all help to minimise the corrosivity/irritancy hazard, reduce the carbonation tendency and improve their compatibilities with epoxy resins. The principle commercial uses for the various modifications are coatings on concrete, mortar, steel, synthetic mortars, sealing and trowelling compounds and concrete repair applications.

As an aliphatic diamine, it is strongly alkaline. When combined with inorganic acids it will give stable alkaline and neutral salts. It reacts with phosgene, aldehydes, epoxy resins, carboxylic acids, ketones and the like. Isomers generally show likely behaviours.

TMD is a free flowing liquid, miscible with water and the usual organic solvents in any proportions at room temperature.

In many respects, it behaves like hexamethylene diamine, but because of its structure it possesses some special properties that make it suitable for a variety of special applications.

Derived from isophorane chemistry, TMD is used in the synthesis of plastics, such as polyamides and polyurethanes. This diamine is used mainly in the production of hardeners for epoxy resin systems. It is also used in the production of corrosion protection agents, emulsifiers, vulcanization accelerators, pesticides, textile auxiliaries, flotation agents, and lubricant additives and among other applications.

As an aliphatic diamine, when compared to other short chain aliphatic diamines, TMD has longer pot-life, without however delaying the curing process. The products cured with TMD will be clear and light stable with flexibility and chemical resistance. It can be used with all types of epoxy resin applications, such as casting resins for electrical use, solvent free and solvent containing lacquers and coatings. It is especially suited for the production of in situ adducts.

It is slightly hygroscopic and tends to form carbamates. It is best stored under exclusion of moisture and carbon dioxide, can be stored in glass, stainless steel and similar containers. It is corrosive to skin and eyes.

2.9.2 -Trimethylhexamethylene Diamine, Cyanoethylated Mixture of Isomers (trimethylhexane -1,6-diamine) (Hardener 4)

It is an aliphaticdiamine from isophorane chemistry . It is a low viscosity liquid with a faint odour of amine. Their low viscosity makes them particularly suitable for special applications. No undesired precipitations occur as a result of carbamate formation. It has a lower reactivity than other well-known epoxy resin hardeners during curing of these resins . Complete curing can occur only from 20 °C upwards.

The long pot-life which can be achieved with this kind of hardeners and epoxy resin system is considered as an advantage for many applications. Hardener may be accelerated by addition of 1-2 parts by weight (pbw) salicylic acid or toluene sulphonic acid referred to 100 pbw epoxy resin and 37 pbw trimethyl hexamethylene diamine.

It is used as hardener for epoxy resins. In this connection the following applications are identified ; coating on concrete, mortar and steel, synthetic mortars, sealing and trowelling compounds [19].

2.9.3 Tertiary Amine (2,4,6 tris di methyl aminomethyl phenol) (Hardener 6)

Generally tertiary amines are accelerators in elevated temperatures for cured systems and give an optimum balance of cure rate, working life and cured mechanical properties. Tris (dimethylaminomethly)phenol contain phenolic hydroxyl groups as an integral part of the structure of the amine. As such they are particularly effective room temperature accelerators/co-curing agents for polyamine-based coatings and adhesive applications.

In all cases the amounts of different t-amines added to a system are determined empirically to achieve the good properties mentioned above. Too much catalyst in the formulations may help achieve faster cure rates but usually at the expense of working-life, embrittlement and/or shrinkage.

2,4,6 tris di methyl aminomethyl phenol is used to accelerate the cure mainly of epoxy/polyamidoamines, in particular of type 1 epoxy/polyamidoamines solvent-based systems and also accelerate other amines (must always be added to the hardener). It will decrease pot life, drying and curing time, more than 5% on resin can decrease flexibility and chemical resistance, if greater quantities are used, the amount of resin must be increased [20].

2.9.4 Triethylene Tetra Amine (Hardener 3)

Aliphatic polyamines, containing 2-8 carbon atoms, including alkylene (C.sub.2 - C.sub.6) diamines, such as ethylene diamine, tetramethylene diamine, hexamethylene diamine, trimethylhexamethylene diamines and the like, polyalkylene(C.sub.2 - C.sub.6) polyamines, such as diethylene triamine, iminobispropylamine, bis(hexa-methylene) triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine and the like, and alkyl (C.sub.1 -C.sub.4)-substituted products of these amines, such as dialkyl (C.sub.1 -C.sub.3) amino-propyl amine, methylimino-bispropylamine and the like; alicyclic or heterocyclic ring-containing aliphatic polyamines, such as 3,9-bis(3-amino-propyl)-2,4,8,10-tetraoxaspiro(5,5) undecane and the like; alicyclic or heterocyclic polyamines, containing 4-15 carbon atoms, such as menthane diamine, piperazine, N-aminoethyl-piperazine, cyclohexylene diamines (such as 1,3-diamino-cyclohexane), isophorane diamine, dicyclohexylmethane diamine and the like; araliphatic poly-amines, containing 8-15 carbon atoms, such as xylylene diamines, tetrachloro p-xylylene diamine and the like; polyamide polyamines, such as condensation products of amines as above with polymerized fatty acids (such as dimer acid); polyether polyamines, described below as high molecular weight active hydrogen atom-containing compounds; dicyandiamides; and so on [7]. Figure 2.2. shows the chemical structure of TETA.

$H_2N\text{-}(CH_2—CH_2\text{-}NH)_3\text{-}H$

Figure 2.2: Chemical structure of TETA [21]

The used product is triethyleneamine (mixture of isomers) for synthesis. It is a clear, yellow liquid which with water forms a crystallized hydrate. The product has an alkaline reaction and is hygroscopic. It is used in chemical industry, for example as an intermediate for the synthesis of, cellulose chemicals and paper auxiliaries, coatings and auxiliaries, synthetic rubber and rubber chemicals, plastics and auxiliaries, auxiliaries for construction industry, auxiliaries for the recovery and processing of oil, coal and natural gas [21].

They are highly reactive primary aliphatic amines with five and six active hydrogen atoms available for cross-linking respectively .12-13 pt phr, the stoichiometric quantity, is required and this will give a room temperature pot life less than an hour. It is widely used in small castings and in laminates because of their high reactivity, they have the disadvantage of high volatility, rigidity and being skin sensitisers. Properties such as heat distortion temperature (HDT) and volume resistivity are critically dependent on the amount of hardener [2].

2.9.5 Meta-xylenediamine (Hardener 2)

Meta-xylenediamine is a low-viscosity, light colour aliphatic polyamine. Prepared by hydrogenation of isophtalonitrile is a di-primary aliphatic amine which behaves more like a di-primary cycloaliphatic amine than an aliphatic diamine. This is most likely due to the rigid nature of the non-conjugated aromatic ring backbone.

It is insensitive to moisture. The high basicity of the unhindered primary aliphatic amine functionality imparts high reactivity and unfortunately a strong tendency to carbonate. This combined with the corrosive and irritant nature means that it is generally used in preadducted form or as a mannich base. Resulting products used for high solids and solvent-free coatings, mastics and flooring applications, are characterised by their excellent subambient temperature cure rates and high cured chemical resistance, suitable for the epoxy resin mortars.

It can also be used as binder for printing inks and varnish systems. Depending on formulation and the epoxy resin chosen, it would have a low level of viscosity making it easy to work, predominantly good adhesion to concrete and sand-blasted steel, very good mechanical properties and generally good resistance to chemicals. It is irritant to eyes and skin, also it mustn't be inhaled. Its smell is like ammonia. It is not soluble in water [22].

2.9.6. Isophorane diamine (xylenediamine) (Hardener 5)

IPDA is a cycloaliphatic diamine based on isophorane chemistry. It is a mixture of two stereo-isomers of 3-aminomethyl-3,5,5-trimethylcyclohexyamine, and is a colourless low viscosity liquid with a faint amine odour.

It can be used in all typical amine reactions, such as reaction with carboxylic acid, phosgene, aldehydes, ketones and epoxies. It is miscible in all proportions at room temperature with a wide range of compounds such as water, alcohols, esters, ethers, ketones as well as many aliphatic, aromatic and halogenated hydrocarbons.

IPDA is a diamine with a special structure due to multiple alkyl substituted cyclohexane ring, amino groups with different reactivity and cis-trans configuration. When compared to other commercially available amines, differences become apparent in the properties of its derivatives and polymer compounds. Its chemical structure is seen on figure 2.3.

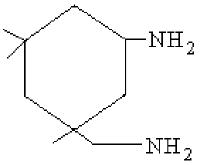


Figure 2.3: Chemical structure of IPDA [23]

It is used as a hardener or curing agent for floor coatings, paving aggregates, and a variety of urethane and epoxy coatings and resins and in the production of lacquers and paints (ships, automobiles), for the production of stacked plastic parts in the construction of aeroplanes and ships and also in the electronics industry and in special adhesives. It has large application in epoxy-based self-levelling and towelable flooring systems, and various civil engineering applications .IPDA is also used in the manufacture of diisocyanates and in composites and polyamides. IPDA provides coatings with high temperature stability and low colour. Other applications include coatings for superior corrosion protection of metal, adhesives and anchoring compounds. IPDA has many other uses based on amine chemistry, such as the production of non-crystalline speciality polyamides with high hardness and optical transparency, used as a chain extender in polyurethanes, as an intermediate in dyes and also used in the manufacture of diisocyanates and in composites and polyamides, mostly used to produce hardeners for solventless, room temperature curing epoxies and as a hardener in heat cured epoxies.

Hardeners based on IPDA have low viscosity, low tendency to form carbamates and humidity resistance. Epoxy systems cured with IPDA based hardeners exhibit excellent chemical resistance, high heat distortion temperatures and colour stability.

Reduces brittleness, provides a weak accelerating effect and helps the hindered amine get through the B-stage. Applications for this low viscosity curing agent type include highly filled screed flooring and coatings applications.

IPDA is slightly hygroscopic and tends to form carbamates by reaction with atmospheric CO_2 [23].

2.10 Structure and Properties of Cured Resins

Being cross-linked, the resin will not dissolve without decomposition but will be swollen by liquids of similar solubility parameter to the cured resin. The chemical resistance is as much dependent on the hardener as on the resin since these two will determine the nature of the linkage formed.

The main skeleton of the resins themselves has generally good chemical resistance. The thermal properties of the resin are dependent on the degree of cross-linking, the flexibility of the resin molecule and the flexibility of the hardener molecule. Consequently the rigid structures obtained by using cycloaliphatic resins or hardeners such as pyromellitic dianhydride will raise the heat distortion temperatures.

The resins are somewhat polar and this is reflected in the comparatively high dielectric constant and power factor for an insulating material [2].

3. APPLICATIONS FOR EPOXY

3.1 General Applications for Epoxy Resins

The applications for epoxy based materials are extensive and include coatings, adhesives and composite materials like carbon fiber and glass-reinforced plastic (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allows cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good to excellent mechanical properties and very good electrical insulating properties, but almost any property can be modified (for example silver-filled epoxies with good electrical conductivity are widely available even though epoxies are typically electrically insulating) [23].

Epoxy resins are usually more expensive than their rivals, such as phenolic resins for coatings or laminates. Therefore, epoxy resins find application because of their superior properties, which include both processing and those of the cured resin .The processing is convenient since it is possible to formulate compositions with the required rheological properties, such as low viscosity, and there is also a wide choice of hardeners so that it is possible to cure at ambient as well as elevated temperatures. Because epoxy resins can be cross-linked without the formulation of low molecular weight products, volatiles are not evolved during cure, and the resins have only a relatively low shrinkage during curing. Their mechanical and electrical properties are superior to other resins and they have good heat and chemical resistance [7].

Epoxy resins can also be used when reinforced with fibers as composite materials. Epoxy resin laminates are of particular importance in aircraft industry. It has been stated that the Boeing 757 and 767 aircraft use 1800kg of carbon fibre/epoxide resin composites for structure purposes per aeroplane. The resin has also been used with Aramid fibres for filament-wound rocket motors, pressure vessels and also in small boats which has a much better performance than traditional polyester/glass fibre composites [2].

Selection of a resin-hardener system can be made by a critical assessment of processing and end-use requirements. It is possible to enhance a desired parameter simply by changing the cure schedule without a change in the initial composition of the resin-hardener system. Thus- it is possible to increase T_g of the cured resin by post-curing. The Young's modulus of epoxy resins is some what lower than that of the phenol formaldehyde (P/F) and unsaturated polyester resins but the tensile strengths are comparable and may be higher. This is because the extensibility, that is the fracture strain, of the epoxy resin is much higher than that of the "brittle" resins. The tensile strength can be significantly affected by cure treatment and the fracture behaviour of epoxy resins should always be considered when an application demands optimum strength. With standard BPA-epichlorohydrin resins the heat distortion temperatures are similar to those of P/F and polyester resins, but with suitable hardener and a post-cure at elevated temperatures it is possible to attain higher T_g and hence higher use temperatures.

Cycloaliphatic resins have very good outdoor ageing properties. This is because, they don't contain aromatic rings which absorb the UV radiation which leads to degradation processes. Also, the chlorine, and other halogen, content of the cycloaliphatic resins is essentially zero and hence these resins have very good electrical properties. By comparison with the P/F and unsaturated polyester resins it would not be possible to assess the superior technical properties of the epoxy resins. Their processing properties offer considerable advantages. The range of hardeners available is one of a major chance since it is possible to formulate a curing system to suit almost every specific requirement. Epoxy resins have very good solvent resistance, which is a major advantage in many applications [7].

3.1.1 Epoxy in Civil Engineering

In civil engineering the consumption of concrete, wood, metal and glass is astronomical. Epoxy resins exhibit excellent adhesion to these materials and therefore have been used widely for surface coatings and for repairments. The most frequent application of epoxy resin in civil engineering include;

- Flooring
- Road and bridge coatings
- Concrete bonding and repair

3.1.1.1 Flooring

Solvent free epoxy systems have been used successfully in coating and flooring applications for many years [25] . In spite of the high initial cost, such floorings have excellent chemical and wear resistance [2].

Epoxy flooring can be formulated to be 100% non-volatile and 100% reactive so that 1 inch thick coatings may be applied in a single application. Floors of industrial premises such as chemical plants and store houses are subject to constant and severe abuse of various forms. Typical examples are chemical spillage, harsh detergent cleaning and heavy frictional wear by vehicles such as forklifts etc. Since floors of such industrial buildings are usually constructed with materials such as concrete, which under adhesive service conditions are likely to gradually and then rapidly disintegrate, epoxy resins have been found to be very useful in aiding the maintenance of such floors, due to their chemical resistance, high mechanical strength and easy application [7].

In formulating a flooring system, the epoxy resin is usually mixed with hardeners, fillers and pigments according to service requirements [7]. The cure of the epoxy resin in flooring systems is often based on mixtures of different amines. Common examples are IPDA and MXDA. To optimise cure, the use of product like Benzyl Alcohol, Salicylic acid and other additives are very common and often required in order to complete cure [25].

Colouring materials can also be added to suit different purposes. Before the application of the resin the surface has to be cleaned and pre-treated with an epoxy or other primer. Depending on the viscosity of the formulated system, it can be applied either by brush, roller, squeegee or trowel. For high viscosity formulations such as those primarily for wear resistance where large quantities of solid filler are added, the material has to be screeded by trowelling. On the other hand, low viscosity formulations for covering continuous floors with normal wear conditions can be applied with a squeegee or plastic comb [7].

Reducing amount of binder improves the abrasion and scratch resistance of cure flooring system. The matt surface perfectly hides application / surface differences, even applied on uneven substrates [25].

Self levelling epoxy flooring compositions are formulated so that their viscosity is low. Epoxy flooring may be classified into three types; 1) seamless flooring, 2) industrial or epoxy concrete and 3) terrazzo flooring

1) Seamless flooring has a low viscosity due to the use of a reactive diluent and can be applied in thickness of 10-60mm. They can be used to coat Portland cement floors, wood or metal after a specific surface preparation before application of the resin.

2) Industrial epoxy flooring or epoxy concrete contains 75-85% particulate filler, usually sand (10-100 mesh). With high filler loadings the viscosity is high and the composition is applied by trowelling with thickness of 3-25 mm (1/8 to 1 inch). These compositions have low shrinkage and may be used to repair cement floors.

3) Epoxy terrazzo floors contain coloured stone or marble chips and a fine particulate filler, such as calcium carbonate, and a re trowelled to give 6-12mm (1/4 – ½ inch) thick coatings. After setting overnight they are wet-ground to a polished terrazzo surface which is readily maintained.

The advantages of epoxy flooring may be summarized as follows;

1. Ease of seamless application, room temperature cure with low shrinkage
2. Excellent adhesion to many substrates
3. Chemical resistant and durable
4. Tough, flexible and abrasion –resistant
5. Dust-free, skid-resistant and readily maintained [7]

3.1.1.2 Road and Bridge Coatings

The resins are claimed to be particular value at road junctions and roundabouts, where severe wear is experienced, but where repairs and maintenance operations must be kept in a minimum level because of the resultant disruption in the flow of the traffic [2].

Epoxy resin coatings have been used to protect and repair road and bridge surfaces. Spalling is a commonly encountered problem on the surfaces of roads and bridges. It is caused by the combination of many different factors such as freeze-thaw cycles, spillage by vehicles, road gritting and de-icing operations.

Epoxy resins that are used for the treatment of these conditions are usually liquids cured by amine hardeners at ambient temperatures. Coal tar is used as extender and often in high proportions in their formulation. When coated onto the structure and cured, the resin formulation forms a film which prevents the spalling of concretes on the road surface and bridge structure. Furthermore, the use of such formulations to seal cracks can significantly slow down their growth by bonding the damaged sections into an integral part. It also limits water penetration into the structure of the bridge. Ingress of water to steel reinforcement or framework causes corrosion. Epoxy resin coatings can give substantial protection against such damage. Some other applications of epoxy resin road and bridge coatings include;

1. Repair of scaling concrete roads with “thin” coatings
2. Repair of asphalt or concrete road surfaces
3. Fuel spillage protection
4. Light-weight surfacing for bridge decks
5. Waterproof membrane between concrete and an asphalt topping
6. Upgrading additive for bituminous surfacing compositions
7. Road marking and coloured surfaces [7]

Epoxy asphalt has been used for the pavement of several bridges in the United States has an excellent performance record. The preliminary tests indicated that the performance of epoxy asphalt was far superior to that of other systems [26].

3.1.1.3 Concrete Bonding and Repair

A restoration project properly executed and using the correct repair products can add years to the service life of a structure. The cost to properly repair a structure is often significantly less than the cost of replacement or further deterioration [24].

Structural epoxies in the form of resin or mortar have been in use for over 35 years for the repair and restoration of concrete and wood members. Modern epoxy adhesives are not sensitive to moisture and may be applied to damp or dry surfaces, and cracks need only be clean of debris and free of standing water. Manufacturers of approved epoxy resin based bonding systems must meet American Society for Testing Materials (ASTM) standards that regulate the modules of elasticity (stiffness of a material to imposed loading) tensile, compressive, and flexural strengths [27].

Use of epoxy resin formulations as concrete bonding and repairing materials finds application over much wider areas than just bridges and roads.

Some of are;

- Bonding medium between fresh and hardened concrete
- Binder of epoxy mortars or polymer concretes
- Producing epoxy –modified concrete and protecting reinforcing bars against corrosion [28]

Virtually, any structure with concrete as its primary construction material will developed cracks with age. Epoxy formulations can be coated onto the surface to prevent the initiation of such cracks and also to repair existing cracks. Structural defects occurring in other materials such as wood, brick and metal can also be repaired by epoxy formulations[7]. And also epoxy modified materials would provide higher durability and bonding strength because of homogenous structure [29].

The excellent adhesion, high cohesion, low shrinkage on cure, absence of volatile solvents and low creep of the resins have led to important applications as adhesives, particularly for metal-to-metal and metal-to-plastics bonding.

As with the surface coating there is a diversity of possible formulations available, selection being dependent on the requirements of the end-product [2].

4. EXPERIMENTAL PART

In this chapter the used materials and then applied tests were introduced. Physical and chemical measurements were applied to characterize the sample and testing the performance.

4.1 Materials

4.1.1 Epoxy Resins

The epoxy resins used in this study are bisphenol A, bisphenol F and bisphenol A/F resin which includes 70 % bisphenol A and 30 % bisphenol F resin.

Epoxy equivalent weight of bisphenol A resin is 194,932 g/ val while epoxy equivalent weight of bisphenol is 171,233 g/val . On table 4.1. general information of used epoxy resins are given.

Table 4.1: General information about epoxy resins used in this study

Epoxy resin	Viscosity (cp)	Density (g/ml)	Epoxy value	Epoxy eq. weight (g/val)
Bisphenol A	16700	1,1577	0,5376	194,932
Bisphenol F	5850	0,8858	0,584	171,233
Bisphenol A/F	9500	1,1543	0,5434	182,475

4.1.2 Hardeners

As previously mentioned six hardeners are determined to be used in this study.

On the table 4.2., main types of used hardeners and the properties they provide are seen.

Table 4.2: General properties of the hardeners used in this study [5, 7, 17].

Name	2,2,4- 2,4,4 Trimethyle-hexamethylene Diamine	Meta-xylenediamine	Triethylene tetra amine	Trimethylhexamethylenediamine, cyanoethylated mixture of isomers	Isophorane diamine	2,4,6 tris di methyl aminomethyl phenol
Type	Aliphatic	Aliphatic	Aliphatic	Aliphatic	Cyclo-aliphatic	Accelerated Cyclo - aliphatic
Properties	*low M.W. *low visc. *high reactivity *strong tendency to carbonate * hydrophobic * moderate compatibility with epoxy resin * long pot life	* low visc. * insensitive to moisture * high basicity * high reactivity * strong tendency to carbonate * good adhesion * good mechanical properties * good chemical resistance	* alkaline reaction * highly reactive * high volatility * high pungency	* low viscosity * lower reactivity * long pot life	* low visc. * humidity resistance * super chemical resistance * colour stability * reduces brittleness	* expense of working-life * embrittlement and/or shrinkage * decrease flexibility and chemical resistance

4.1.3 Reactive Diluents

Three types of reactive diluents are used in this study. They are mono functional, difunctional and trifunctional epoxy based reactive diluents.

Monofunctional reactive diluent used in this study is glycidylether C12-C14 alcohol, difunctional reactive diluent is 1,6 Hexanediol diglycidylether and finally trifunctional reactive diluent is trimethylopropane glycidylether. On table 4.3., properties of reactive diluents are given.

Table 4.3: Properties of reactive diluents used in this study

Functionality	Density (g/ml)	Viscosity(cp.)	Epoxy eq. weight(g/val)
monofunctional	0,8858	10	289,412
difunctional	1,0675	23	142,857
trifunctional	1,1543	149	142,045

4.1.4 Aggregate

Aggregate mixture was consisted of 64% silica sand in the range of 0,075- 4 mm and 14% of fine material.

4.1.5 Benzyl Acohol

It is a common solvent for epoxy resins. It is also called phenylmethanol or phenylcarbinol. It was used as activator for Hr 4 and Hr 5 mixtures.

4.2 Rheological Measurements

4.2.1 Viscosity Measurements

Control of the processing of epoxy resins requires information on their rheological properties. For the liquid resins which may have high viscosities it is very difficult to mix with hardeners so that an uniform molecular dispersion is obtained. With some hardeners, reactions occur even at room temperature and hence the viscosity increases before mixing is complete and microgelation may occur and of course locally the epoxy/hardener stoichiometry is out of balance. Even with hardeners which require elevated temperatures it is often necessary to warm the resin to reduce its viscosity so that a molecular mixture can be obtained. Some of the morphological features observed in cured epoxy resins can be attributed to inefficient mixing of the hardener with the epoxy prepolymer. For many applications such as casting, undiluted epoxy adhesives and laminating resins it is essential that their viscosity during fabrication is low. Also, air bubbles which rise to the surface very slowly, if at all, may be very troublesome when the viscosity increases due to their onset of cure.

Viscosity depends on the molecular weight, molecular weight distribution, chemical constitution of the resin and the presence of any modifiers or diluents[2]. For ‘compounded’ resins which are liquid at room temperature, their viscosity is measured without dilution. Solution viscosities can be measured by bubble viscometers such as the Gadner-Holdt tubes, capillary viscometers or instrumentally with a spindle viscometer such as Brookfield. For these measurements the concentration of the solution and its temperature must be kept to specified values to obtain satisfactory measurements [8].

The structure of the epoxy resin affects its viscosity, for example the aromatic, bisphenol A type epoxy resins have higher viscosities than the equivalent cycloaliphatic which are themselves higher than linear alophatic. [8]

In this study, the viscosity measurements are done with a Brookfield viscometer, according to the laboratory hand book. The used materials are; Brookfield viscometer (LVT), a container for 600 ml and thermometer. In figure 4.1. Brookfield viscometer is seen.

Figure 4.1: LVT Brookfiled Viscometer

Sample is taken to the container and is adjusted to the determined heat by the water bath. Then the container is placed under the device, test is started with the determined mile and speed, is waited until a stable value is seen on the indicator. At the same time, this operation can be done with the container in a constant degreed water bath to prevent the heat changes if needed.

Attention has to be paid to prevent the formation of air bubbles. They can cause the continuous change of the indicated value or the wrong result.

The value on the indicator is multiplied with a number which is determined by the mile and period used. So the viscosity value is gained with the centipoises unit.

4.2.2 Flow Table Measurements

The test is done according to hand book. The flow table value of fresh mortar sample is determined by the measuring the radius of average flow of the sample on the flow table, by placing the mortar sample with the help of a die which is a cut cone and has a determined form and scale . The cut cone die must be with the height of 60 mm ± 0.5 mm, inner radius of below part must be 100 ± 0.5 mm and the inner radius of top part must be 70 ± 0.5mm. After placing the sample into the die on the flow-table, the die is pushed upwards to let the sample spread.

The volume of the fresh mortar sample has to be at least 1,5lt. Mixing time has to be counted after all components are added. A negative development during the mixing has to be noted. Mix has to be done with a spatula with hand for 5-10 seconds without creating an extra mixing effect to prevent “fake setting of concrete”.

Experiment is done by following the steps below;

1. Glass sheet has to be placed over the flow table with the help of pincers.

2. Glass sheet and cone must be wetted with a piece of moist cloth.

3. Cone must be placed at the middle of glass sheet.

4.To fill the cone easier a filling cap is used.

5. Prepared mix is filled in the cone with two layers, each is squeezed 15 times with mallet cone is pressed over glass sheet with other hand during filling.

6.Filling cap of cone is removed.

7.The top part of the mortar in cone is straightened with the help of a spatula.

8. If there are mortar lefts, they must be removed from the sheet with a piece of moist cloth.

9.The water drops around the below part of cone must be taken with a piece of cloth.

10.Cone must be taken over perpendicularly.

11.After the flow the average values of the measurements which are perpendicular to each other are calculated.

12.Measurement values are recorded in mm.

Calculation and the interpretation of the experiment results;

If the average value of two samples is not deviate more than %10, this value can be taken as average flow value. If two experiment results deviate more than 10% from average value, experiment must be done again with a new sample.

4.3 Epoxy content

Epoxy content is the commonest analytical measurement that is carried out on uncured epoxy resins [8]. Epoxy equivalent is defined as the weight of the resin in grams which contains one gram equivalent of epoxy. Epoxy value is also employed and represents the fractional number of epoxy groups contained in 100gr of resin.[15] Epoxy equivalent is used in calculating the optimum curing agent quantity [15]. According to laboratory hand book the epoxy value and epoxy equivalent weight measurements are done with titrometer by the way told below. The needed materials are ; a balance with 0,1 mg sensitivity, titrometer (798 MPT Titrino), electrode no; 6.029.100, magnetic stirrer (728 Stirrer), thermal magnetic stirrer, 1 N $HClO_4$, Tetra Ethyl Ammonium Bromide (TEAB) and acetic acid. In figure 4.2. titrometer is seen.

Figure 4.2: 798 MPT Titrino titrometer

Generally 0,1 g sample is weighed on the titration container which is with 0,1 mg sensitivity and 6.1415.250 numbered saving . 6 g of TEAB and nearly 100 ml acetic acid is added, then is stirred with thermal mechanical stirrer until all TEAB is dissolved. After the dissolvation has completed, is placed under the titrometer with the proper titration bottle and electrode. Saving protection number 6.1414.010 is placed.

“Epoxy” has to be chosen from the “user method” and then the test is started. At the end of the test, the result can be taken by the automatic calculation. The written results can be taken from the printer of titrometer at the same time.

Before the weightening the sample, a witness try is done. Equation 4.1. is for calculating the appropriate sample quantity.

$$\text{Appropriate sample quantity} = \frac{0{,}8}{\text{Approximate epoxy value}} \tag{4.1}$$

4.4 Pot-life

Pot-life is the time spent for gaining a rigid mixture of epoxy resin and hardener. This test can be done at the desired temperature. For this study, pot-life tests were done comparatively by changing the hardener types at room temperature. So the pot-life times were compared according to hardener types.

Hardener quantity determination is done by some stoichiometric calculations with the equation 4.2., equation 4.3., equation 4.4., equation 4.5., equation 4.6., equation 4.7. and equation 4.8. depending on the hardener type.

$$\text{Mixing ratio (phr)} = \frac{\text{A.H.E.W. (Active Hydrogen Equivalent Weight)}}{\text{Epoxy equivalent}} \times 100 \tag{4.2}$$

a) Polyamine Curatives

$$\text{A.H.E.W.} = \frac{\text{Amine molecular weight}}{\text{No. of activated hydrogen}} \tag{4.3}$$

b) Polyamide amine curatives

$$\text{Phr (Per hundred r.} = \alpha \times \frac{\text{A.H.E.W. (Active Hydrogen Equivalent Weight)}}{\text{Epoxy equivalent weight}} \times 100 \tag{4.4}$$

α Value		
	Bending strength	0,9 ~ 1
	Bending strength	0,7 ~ 0,8
	Compressive strength	0,6 ~ 0,7
	Adhesion strength	0,8 ~ 1,4
	H.D.T.	1,0

c) Anhydride curatives

$$(\text{phr}) = C \times \frac{\text{A.H.E.W. (Active Hydrogen Equivalent Weight)}}{\text{Epoxy equivalent weight}} \times 100 \tag{4.5}$$

C= 0,85 (without accelerator)
C= 0,55 (when using acid as accelerator)
C= 1,0 (when using tertiary-amine as an accelerator)

$$\text{Anhydride A.H.E.W.} = \frac{\text{Molecular weight of Anhydride}}{\text{No. Of anhydride functionality}} \tag{4.6}$$

d) Amine/Epoxy Adduct Curatives

$$(\text{Amine } M \text{ mole } (Mw) \text{ / Epoxy } M' \text{ mole } (Mw') \text{ system}) \tag{4.7}$$

$$\text{Adduct A.H.E.W.} = \frac{\text{Amine } Mw \times M \times \text{Epoxy } Mw' \times M'}{\text{Activated hydrogen No of Amine} \times M - \text{Functionality of Epoxy} \times M'}$$

e) Amines Mixture Curatives (4.8)

$$\frac{\text{Amount of Amine A}}{\text{A.H.E.W. of Amine A}} + \frac{\text{Amount of Amine B}}{\text{A.H.E.W. of Amine B}} = \frac{100}{\text{A.H.E.W. of mixture(g/eq.)}}$$

[30]

From this equations and pre-experiments, optimum quantities for each hardener are calculated and shown below. For hardener 4 and hardener 5, pot –life times was very high so the usage of an activator is needed. This activator was benzyl alcohol and used 30 % for hardener 4 and 10 % for hardener 5. Table 4.4. shows the quantities of hardeners for 100g resin in this study.

Table 4.4: The quantities of hardeners per 100g resin that are used in this study

Hardener type	Quantity (g)
Hr 1	40
Hr 2	34
Hr 3	13
Hr 4	37,2
Hr 5	42,6
Hr 6	20

Also the concentration of the epoxy resin is important for determining the hardener quantity [31].

4.5 Hardened State Measurements

These measurements were applied to the three component hardened systems which include epoxy resin (can be with or without reactive diluent addition), hardener and sand. Tests were applied to samples after a desired time of curing.

4.5.1 Bending (Flexural) and Compressive Strength

A mixture of resin, hardener and sand, according to the producers instructions and the stoichiometric ratios was prepared. Resin quantity is nearly 250 g in the mixtures while the hardener quantities were proportional with the quantities used in pot-life tests for 100g resin and the amount of sand is 1400 g which was fixed. These rates of usages are depend on the producers instructions. This mixture was placed in oiled dies appropriately, showed in figure 4.4. Two groups of experiments were done, one group was conditioned for one days and broken, the other group was conditioned for 14 days and broken. Each set is consisted of 3 prisms. Before the experiment each prism was weighted and its dimensions were measured with a calliper to determine the dimension changes. Then bending strength is measured with Alsa Laboratory Equipments under 2 kN load application. Equipment is showed in figure 4.5. In figure 4.4 samples in oiled dies are shown.

Schematic representation of this flexural loading is shown on figure 4.3.

Beam bending is analyzed with the Euler-Bernoulli beam equation. Equation 4.9. is the classic formula for determining the bending stress in a member and equation 4.10 is used for determining the compressive strength.

$$\sigma = \frac{My}{I_x} \tag{4.9}$$

- σ is the bending stress
- M - the moment at the neutral axis
- y - the perpendicular distance to the neutral axis
- I_x - the second moment of inertia about the neutral axis x [23]

After bending test, 25kN load was applied to each broken piece for compression test. All the load values are recorded and an average value for bending and compressive strength is calculated for each set.

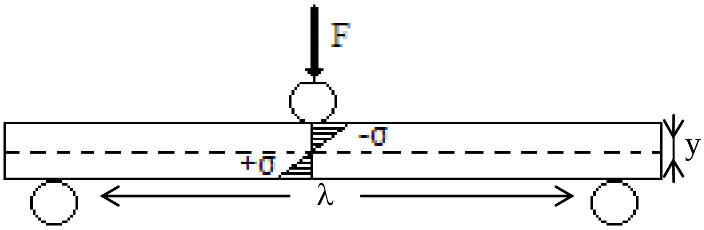


Figure 4.3: Schematic show of flexural loading.

$$f_c = \frac{P}{A_0} \tag{4.10}$$

P represents load (MPa) and A_0 is cross-sectional area (mm^2) .

Figure 4.4: Samples in oiled dies

Figure 4.5: Alşa Laboratory Equipment on which the bending and compression tests were made

4.5.2 Durability-Chemical Resistance Tests

This test is used for determining the chemical resistance of mortars over desired chemicals. First the mortars are prepared with addition of 3% pigment material into sand. Mixed samples are casted as plates with dimensions nearly 3cm x 5cm. They have to be waited for 14 days. Then the chemicals that are going to be used for experiments are prepared and taken into jars. Sample plates are placed in the jars including chemicals with some parts of the samples are out of the jar. Samples are observed daily and the effects of chemicals are recorded and graded with letters which are ;

A- No damage

B- Low damage

C- Moderately damaged

D- Colour fading

E- Hardly damaged.

The chemicals chosen for this test are ;

- 15 % Lactic acid
- 20 % Formic acid
- Alcohol
- 37 % Formaldehyde.

This test method is the modified form of TS EN 12808-1 “Determination of chemical resistance of reaction resin mortars”, but the sample dimensions are not identified unlike in TS EN 12808 and so the calculation part is neglected.

The chosen samples for this experiment are basic epoxy resins which are Bisphenol A, Bisphenol F and Bisphenol A/F with hardener 3 (TETA) and Bisphenol A resin with other 4 hardeners except hardener 6 (Tertiary amine), Bisphenol A, hardener 3 and reactive diluents mixtures with different kinds and with different ratios which are previously used in other experiments in this study. The chosen samples for this test are showed on the table 4.5.

Table 4.5: Chosen samples for chemical resistance test

Sample No.	Coding	Sample
1	R3	RF + Hr.3. + Sand
2	R1	RFA30 + Hr.3.+ Sand
3	R2	RA +Hr.3 + Sand
4	R15	RA (%95) + RDMF (%5)+ Hr.3 + Sand
5	R7	RA (%90) + RDMF (%10)+ Hr.3 + Sand
6	R8	RA (%90) + RDDF (%10)+ Hr.3 + Sand
7	R9	RA (%90) + RDTF (%10)+ Hr.3 + Sand
8	R16	RA (%85) + RDMF (%15)+ Hr.3 + Sand
9	HR3	RA + Hr.1 + Sand
10	HR1	RA + Hr.2 + Sand
11	HR13	RA + Hr.4 + Sand
12	HR9	RA +Hr.5 + Sand
13	HR11	RA + Hr.5 + % 10 Activator + Sand
14	HR10	RA (%90) + RDDF (%10)+ Hr.5 + Sand
15		RA (%95) + RDTF (%5)+ Hr. 3 + Sand

This choice is made according to results of compressive and bending strength tests and properties of hardeners and resins.

4.5.3 Pull-off Adhesion Test

This test is modified from EN 1542 for rigid materials with thick layers like grouts, mortars products and systems forth protection and repair of concrete structures. This test method is for measurement of adhesion strength by pull-off. It specifies a test method to measure the tensile adhesion strength of grouts, mortars, concrete and surface protection systems.

The method of test is by direct dolly pull-of using a steel dolly bonded to the surface of the repair system, with test area having been defined by coring through the surface.

Dimension of the standard concrete substrate/specimen : 300 x 300 x 100 mm. Producer ca use also concrete specimens with the dimension of 400 x 400 x ≥ 40 mm additional to the standard. The surface must be sandblasted according to EN 1766. The quality concerning strength according EN 1504. Dimension of dolly : diameter 50 mm, thickness 20 mm.

The product to be tested is applied according the manufacturers instruction, as one layer system or as a multi-layer system.

Base concrete must have at least 40 mm thickness, must have moisture content lower than 3 % (carbure method) and must have water absorption value between 0.5cm^3 and 1.5 cm ^{3} after 4 hours when measured with the method explained below.

Water content measurement is done with the method explained below;

a) A degreed glass measurement tube is stuck (Carsten Tube) with an appropriate filling paste to the concrete base.

b) After the paste is put in order, tube is filled with water to its maximum level.

c) Water degree is recorded in every 60 minutes in total test time of 4 hours and absorption is graphed as a function of time.

d) One reference taken from each pile are tested on concrete at least 3 times.

Adhesion strain strength must be minimum 1.5 N/mm^2. Adhesion strain strength must be measured by sticking the plate which has at least 5 cap to concrete base with an adhesive such as epoxy resin directly and this measurement must be done by applying a force with a constantly increasing speed of (250 ± 50) N/s .

Experiment surface must be like a surface provided by a wooden strike board and must be dustless and clean during experiment.

Concrete base must be produced by the procedure told below;

- Binder : Portland cement type appropriated EN 197 (TS 19), CEI 42,5 R (PÇ 42,5)
- Aggregate : Pebble sand with maximum particle size 8 mm, having the continuous classification curve between A and B.
- Mixing ratio of binder and aggregate 1:5 in mass.
- Smallest particle ingredient of ready mixed concrete per m^3: 500 kg/m3 ready cement. Concrete must imply very small particles to provide proper workability and to have close structure. This very small particle contents must be made of cement and up to 0,125 mm particle size aggregate.
- Water/Cement ratio : 0.5
- Production : Using a die which would give out any material vertical or horizontal n the die must be avoided.
- Squeezing : On a vibration table, 90 seconds at 50 Hz.

- Conditioning : Must be conditioned 24 hours at (20 ± 2) °C standard conditions after 6 days of water immersion and after that must be conditioned again for 21 days with each plate placed separately vertical.

To prepare substrate by sandblasting, then cleaning under running water before the substrate will be applied with the repair product or system;

- For a bond test on wet surface, the cured substrate shall be immersed in water for a minimum of 7 days/21 ± 2 °C . Remove the substrate and san upright at Standard climate of 21 ± 2 °C and 60 ± - 10 °C % R.H. for 30 min.

For a bond test on dry surface, the specimens shall cure according to the producers instructions or 7 days at 23 ± 2 °C / 50 ± 5 % R.H. In this study the specimens were conditioned for 7 days. Immediately before applying the product, clean the substrate surface using a soft bristled brush. Figure 4.6. shows the plan of specimen, dolly locations and cross section of test plate .

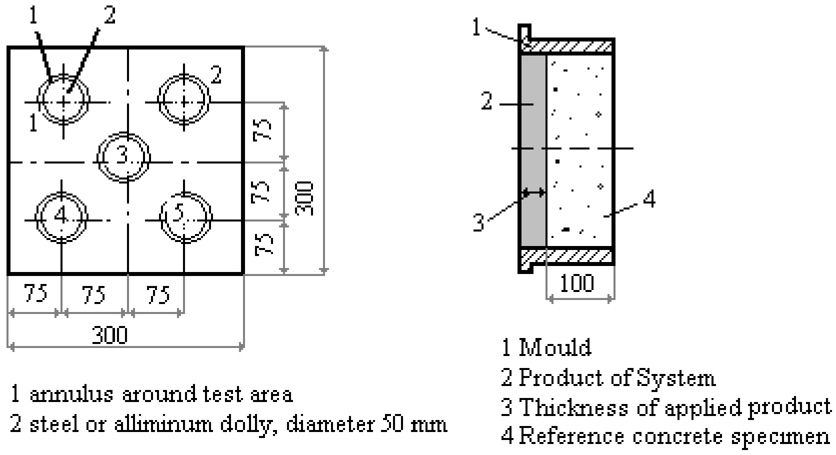


Figure 4.6: Plan of specimen for pull-off test, showing dolly locations and cross section of test plate [33]

For core drilling, drill through the repair product or system to a depth of 15 ± 5 mm into the concrete substrate. The total drill-in depth is calculated by the equation 4.11.

$$d_i = d_d + (15 \pm 5) \qquad (4.11)$$

where ; d_i Total drill in depth

d_d Thickness of mortar layer in mm

Apply thin layer of adhesive between dolly and substrate. No adhesive shall penetrate into the clearance made by coring barrel.

A minimum of 1 test specimen is required for each repair product or system from which 5 bond tests shall be carried out.

A pull-off test equipment complying with EN 24624 with a pulling capacity sufficient to cause tensile bond failure of the specimen is required. The accuracy shall be within ±2 %. A capacity of 10 kN is sufficient for most applications.

Specimens must be conditioned at 23 ± 2 °C /50 ± 5 % R.H. for not less than 24 hours prior to test unless otherwise agreed by the interested parties, e.g. for testing at high or low temperatures.

Increase the load continuously and evenly at a rate of 0.05 ± 0.01 MPa/s until failure occurs. The load at failure must be recorded and the type of the failure must be described.

Tensile adhesion strength calculation is done as told below;

- Tensile adhesion strength is calculated with equation 4.12 to the nearest 0.1 MPa/s for each test assembly .

$$f_h = 4F_h / \pi D^2 \tag{4.12}$$

where ; f_h is the bond of the specimen in MPa/s

F_h is the failure load in N

D is the mean diameter of the specimen in nm

The mean tensile adhesion strength shall be determined from a minimum of 3 test results.

Determine the types of failure from a visual assessment as follows;

A	Cohesion failure in the concrete substrate
A/B	Adhesion failure between substrate and first layer e.g. primer, bonding agent.
B	Cohesion failure in the first layer.

Etc. as defined by the particular product or system under test.

-/Y	Adhesion failure between last and adhesive system layer (to bond dolly).
Y	Cohesion in adhesion layer (to bond dolly).
Y/Z	Adhesion failure between adhesion layer and dolly (which is Z).

Figure 4.7. shows the failures mentioned below .

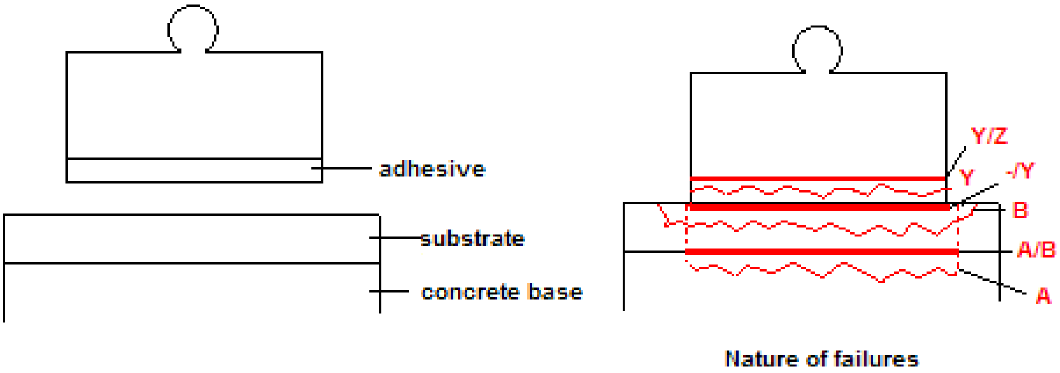


Figure 4.7: Nature of the failures shown on the scheme.

Is the failure a combination of these, a visual inspection shall be made to find the % of each type of failure, based on the surface area, e.g.

Failure A → 40 %

Failure A/B → 10 %

Failure B → 50 % [33]

5. RESULTS AND DISCUSSION

In this chapter the test methods and conditions are stated, the results of this experiments are showed and results are discussed.

5.1 Rheological Measurements

5.1.1 Viscosity

Viscosity measurements are done both for characterizing and comparing. For this purpose, firstly the viscosity of resins and reactive diluents are measured separately. And then reactive diluents with different functionalities (monofunctional, difunctional and trifunctional) are added to epoxy resins with the rates of 5, 10 and 15 %. This measurements are done according to laboratory hand book with a Brookfield viscometer (LTV) . Results are recorded and materialized on a graph. The performance differences of reactive diluents according to their functionality can be observed.

When the results are examined it can be seen that mono functional reactive diluent is more effective than the trifunctional and difunctional reactive diluents, and difunctional reactive diluent is more effective than trifunctional reactive diluent.

Bisphenol A resin has the biggest value and Bisphenol F has lowest viscosity value in this three resin types. When the reactive diluent ratio in resin mixtures, viscosity decreases as expected. Results are placed on the table 5.1. below and showed on figure 5.1.

Table 5.1: Viscosity values of epoxy resins with 10% addition of various reactive diluent types

Functionality and quantity	Resin Type and Viscosity (cp.)		
	RA	RF	RFA
10 % monofunc.	2000	1100	1150
10 % difunct.	2600	1200	2400
10 % trifunct.	3700	2800	3200

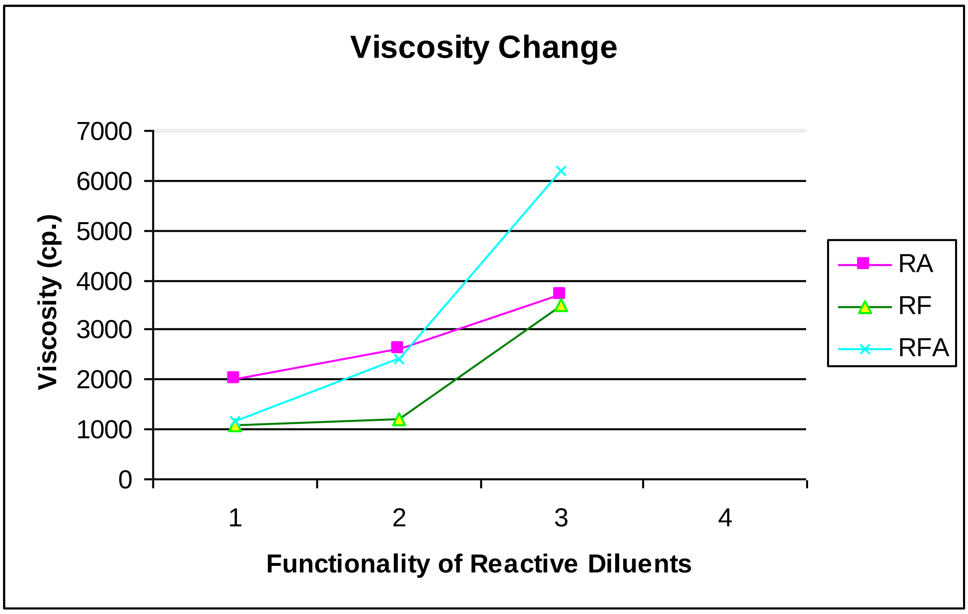


Figure 5.1: Viscosity change upon functionality of reactive diluents with 10% reactive diluent addition.

As it is mentioned above, this graph shows that as the functionality of the diluent increases its efficiency for decreasing viscosity, decreases. Viscosities of resin mixtures are shown on table 5.2. In figure 5.2., viscosity change of bisphenol A resin with different quantities of monofunctional reactive diluent addition can be seen.

Table 5.2: Viscosities of resin mixtures

Resin Mix	Viscosity(cp.)
RFA30	9500
RA	16700
RF	5850
RFA30 (% 90)+ RDMF(%10)	1150
RFA30 (% 90)+ RDDF(%10)	2400
RFA30 (%90)+RDTF (%10)	6200
RA (% 90)+ RDMF(%10)	2000
RA (% 90)+ RDDF(%10)	2600
RA (%90)+RDTF (%10)	2440
RF (% 90)+ RDMF(%10)	1100
RF (% 90)+ RDDF(%10)	1200
RF (%90)+RDTF (%10)	3500
RFA(%95)+RDMF (%5)	4550
RFA(%85)+ RDMF (%15)	900
RA (%95)+RDMF (%5)	4700
RA(%85)+RDMF (%15)	800
RF(%95)+RDMF (%5)	1900
RF(%85)+RDMF (%15)	540

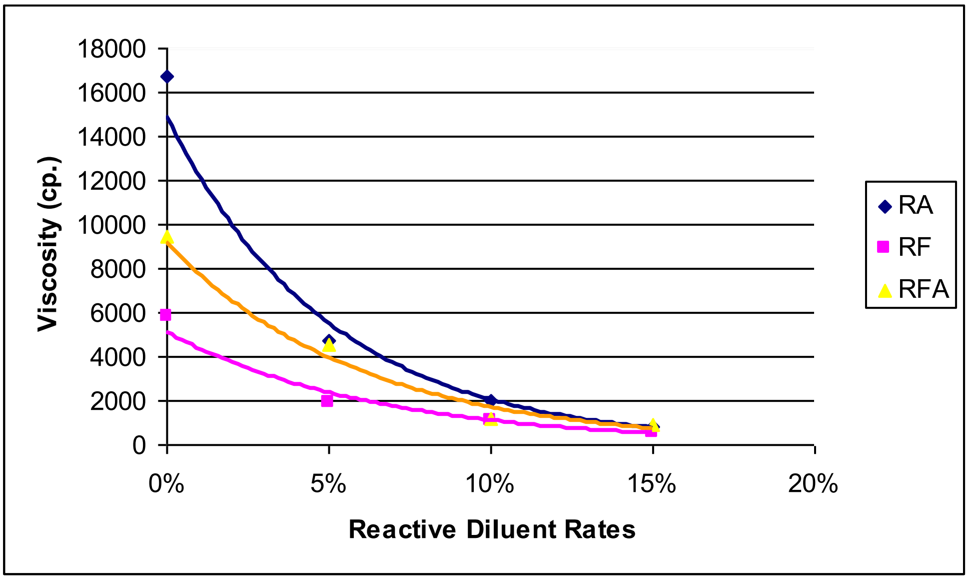


Figure 5.2: Viscosity change of resins with different quantities of monofunctional reactive diluent addition

5.1.2 Flow Table Measurements

Flow –table measurements are based on viscosity. As it is expected the biggest results are obtained from the mixtures with the lowest viscosity. Bisphenol F resin has lowest viscosity among the epoxy resins generally, and with the addition of mono functional reactive diluent in highest ratio that is used in this study which means 15% was resulted in lowest viscosity and surely also highest flow-table measurement in all groups. Figure 5.3 shows the negative correlation between viscosities of pure samples and flow table values of hardener 3 added versions of same mixes.

It must be considered that the viscosity measurements are just applicable to pure resin or resin and reactive diluent mixture, no hardener addition can be done since it can cause curing during measurement. But on the other hand flow-table measurements can be done to both mixtures. Hardeners are used in different quantities which are determined by stoichiometric calculations depending on active hydrogen equivalent weight of hardener, as previously touched. So, it is obvious that the hardener quantity will affect the flow of mixture depending on the type of it.

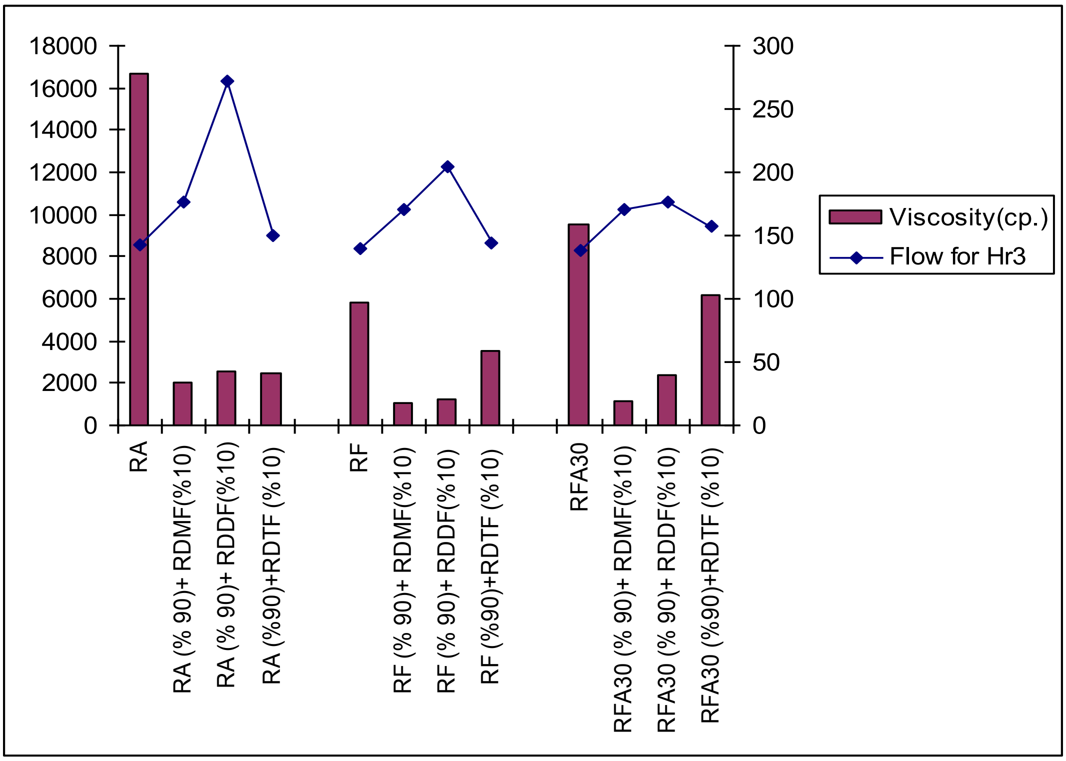


Figure 5.3: Viscosities of pure samples and flow table values of hardener 3 added versions samples.

Also for the Hr.5 and Hr.4, benzyl alcohol can be used as an activator with the ratios of 10% and 30% for some mixtures, which is another point affecting the flow. For example, while Hr.3 is used 32 g, the weight of Hr.4 and 30 % activator is 67,2 g in a nearly 250g resin, when the rates of hardeners in mixture is considered the difference is obvious. As this example indicates, these two samples has the lowest and highest flow values respectively in their groups. On table 5.3, flow-table measurements are given.

Flow table comparison is done according to flow area change with respect to the initial area (5.1).

$$\psi = \frac{A - A_0}{A_0} \tag{5.1}$$

Table 5.3: Flow table measurements.

Resin Mix	Flow (mm)	ψ	Resin Mix	Flow (mm)	ψ
RFA30+HR 6	178	216	RFA30 + HR 3	138	90
RA+HR 6	148	119	RA + HR 3	142	101
RF+HR 6	191	261	RF + HR 3	139	93
RFA30 (% 90)+ RDMF(%10) +HR 6	212	349	RFA30 (% 90)+ RDMF(%10) +HR 3	170	189
RFA30 (% 90)+ RDDF(%10) +HR 6	192	269	RFA30 (% 90)+ RDDF(%10) +HR 3	176	209
RFA30 (%90)+RDTF (%10) +HR 6	206	324	RFA30 (%90)+RDTF (%10) +HR 3	157	146
RA (% 90)+ RDMF(%10) +HR 6	204	316	RA (% 90)+ RDMF(%10) +HR 3	177	213
RA (% 90)+ RDDF(%10)+ HR 6	194	276	RA (% 90)+ RDDF(%10) +HR 3	272	639
RA (%90)+RDTF (%10) + HR 6	178	216	RA (%90)+RDTF (%10) +HR 3	150	125
RF (% 90)+ RDMF(%10) +HR 6	195	280	RF (% 90)+ RDMF(%10) +HR 3	171	192
RF (% 90)+ RDDF(%10) + HR 6	205	320	RF (% 90)+ RDDF(%10) +HR 3	205	320
RF (%90)+RDTF (%10) +HR 6	207	328	RF (%90)+RDTF (%10) +HR 3	144	107
RFA(%95)+RDMF (%5) +HR 6	197	288	RFA30 (%95)+RDMF (%5)+HR 3	171	192
RFA(%85)+ RDMF (%15) +HR6	224	401	RFA(%85)+ RDMF (%15) +HR 3	201	304
RA (%95)+RDMF (%5) + HR 6	194	276	RA (%95)+RDMF (%5) +HR 3	174	202
RA(%85)+RDMF (%15) +HR 6	233	442	RA(%85)+RDMF (%15) +HR 3	196	284
RF(%95)+RDMF (%5) +HR 6	195	280	RF(%95)+RDMF (%5) +HR 3	175	206
RF(%85)+RDMF (%15)+HR 6	209	336	RF(%85)+RDMF (%15) +HR 3	204	316
RA + HR 2	195	280	RA + HR 5	182	231
RA+RDMF (10%) + HR 2	222	392	RA+RDTF (10%) + HR 5	202	308
RA +RDDF (10%)+ HR 2	225	406	RA +RDDF (10%)+ HR 5	215	362
RA+RDTF (10%) + HR 2	193	272	RA+RDMF (10%) +HR 5	185	242
RA + HR 1	194	276	RA +HR 5+ 10%Act.	204	316
RA+RDMF (10%) + HR 1	221	388	RA+RDMF(10%)+HR 5+10%Act.	226	410
RA +RDDF (10%)+ HR 1	221	388	RA+RDDF (10%)+ HR 5+ 10% Act.	224	401
RA+RDTF (10%) + HR 1	203	312	RA+RDTF (10%)+HR 5+10%Act.	215	362
RA (100 +HR 4	185	242	RA (100)+ HR 4+ 30% Act.	224	401
RA+RDMF (10%)+HR 4	203	312	RA+RDMF (10%)+ HR 4+ 30% Act.	229	424
RA+RDDF (10%) +HR 4	218	375	RA+RDDF (10%) + HR 4+ 30% Act.	242	485
RA+RDTF (10%) +HR4	196	284	RA+RDTF (10%)+ HR 4+ 30% Act.	232	438

Figure 5.4 shows the viscosity and flow ratio relation of samples including hardener 6 and figure 5.5 shows the viscosity and flow ratio relation of samples including hardener 3.

Figure 5.6 shows the comparison of flow table results with the formula given above, for the samples including Hr 3 and Figure 5.7 shows the comparison of flow table results of the hardeners and the mixtures with 10% monofunctional reactive diluent addition. Figure 5.8 shows the pot-life comparison of resin types according to functionality of reactive diluent.

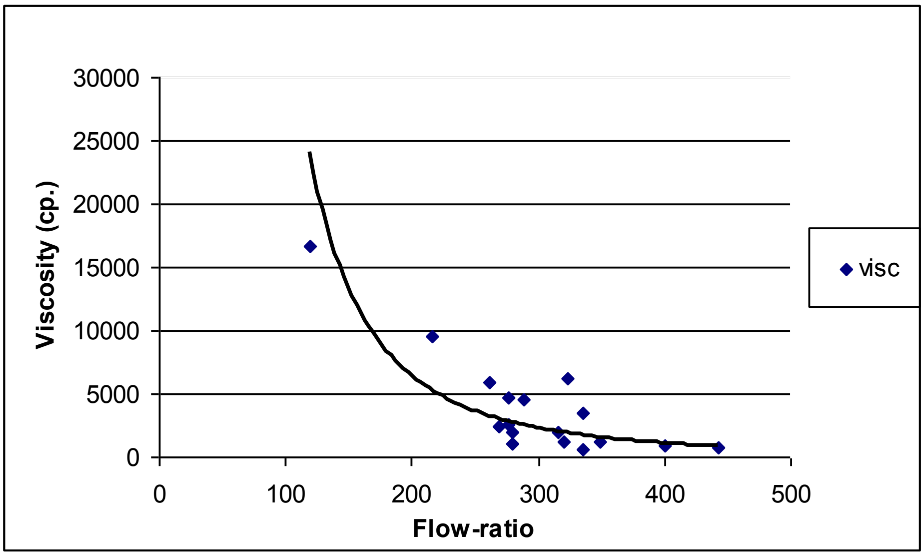


Figure 5.4: Viscosity and flow ratio relation of samples including hardener 6.

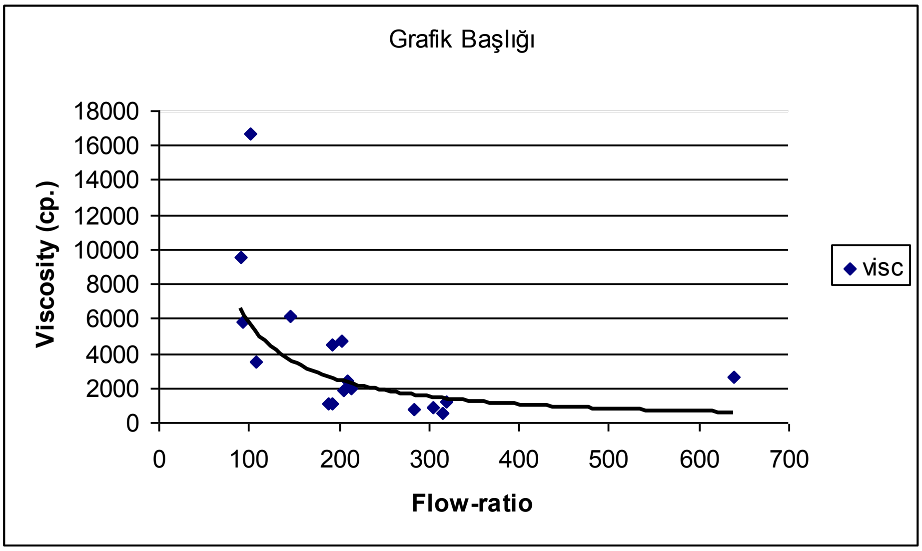


Figure 5.5: Viscosity and flow ratio relation of samples including hardener

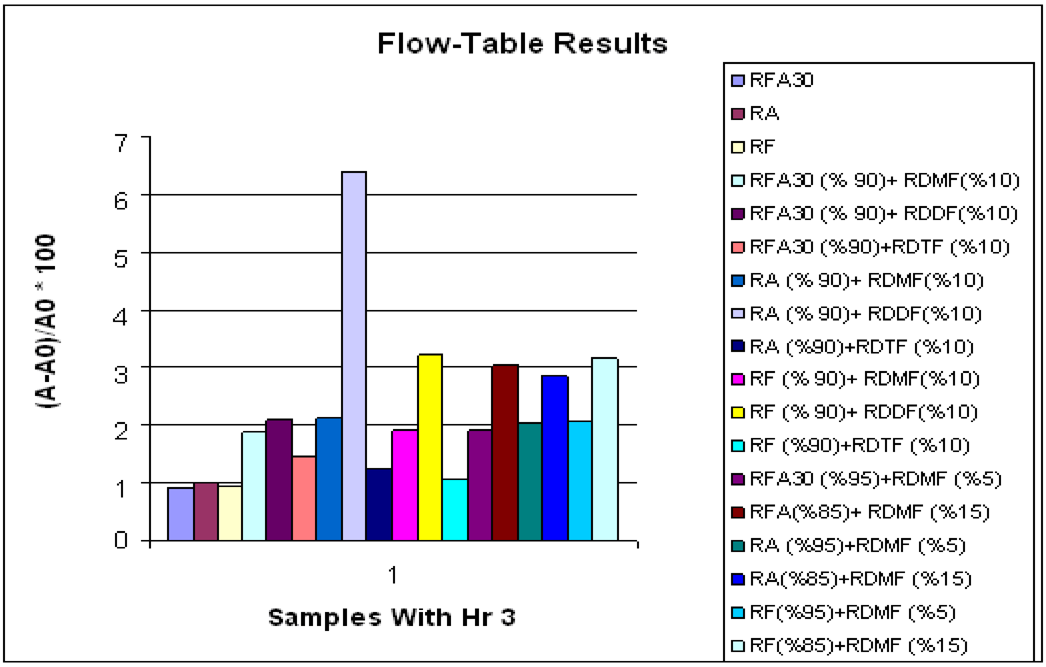


Figure 5.6: Comparison of flow table results with the formula given above, for the samples including Hr 3.

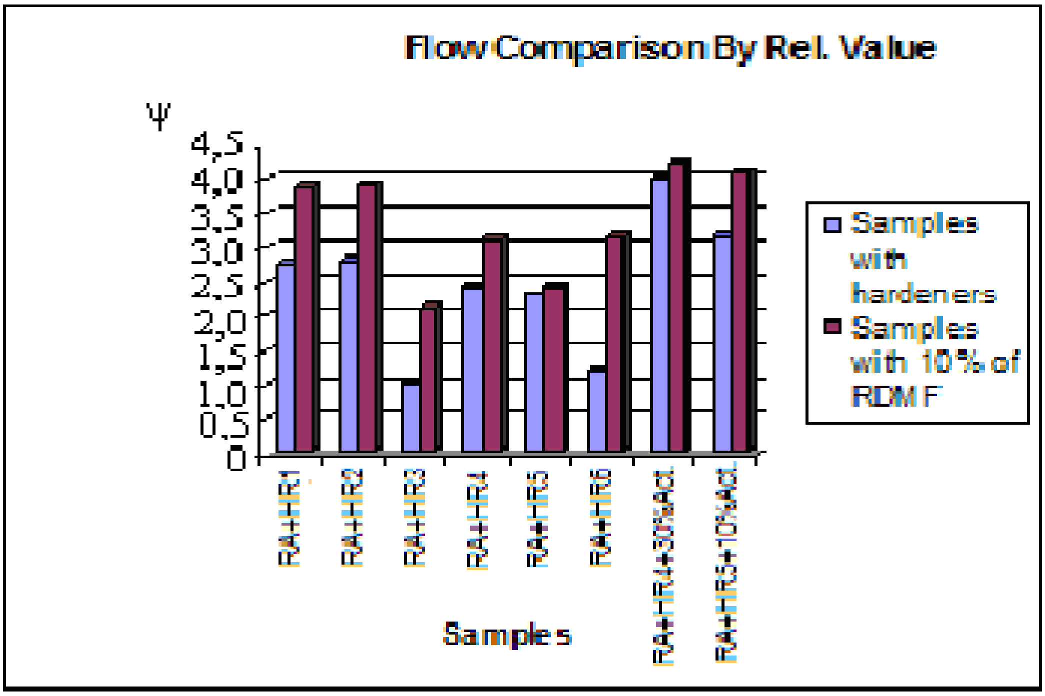


Figure 5.7: Comparison of flow table results of the hardeners and the mixtures with 10% monofunctional reactive diluent addition.

5.2 Pot –life

Pot-life tests were applied to a great number of samples. Even before the real experiments a lot of trials are done to reach optimum pot-life times and determine the optimum hardener quantity. The results of this pre-studies are given on Table 5.4. According to these trials it was determined to add benzyl alcohol to Hr 4 and Hr 5 to increase the performance, 10% of activator addition was enough for Hr 5 while it did less effect on Hr 4. So the determined activator quantity for Hr 4 was 30%. Final experiment results are given on table 5.4.

If pot-lives are compared according to hardener types, a sequence like below is seen;

Hardener 3 < Hardener 1 < Hardener 6 < Hardener 2 < Hardener 5 < Hardener 4.

This sequence is valid for the mixtures with out activator addition. If the samples with activator are added to list, sequence for pot-lives is ;

Hr 3 < Hr 1< Hr 5 + 10 %Act.< Hr 6 < Hr 4 + 30 % Act.< Hr 2 <Hr 5 < Hr 4 .

If the reactive diluents performances are compared, generally lowest pot-lives are achieved by difunctional reactive diluent while the highest pot-lives are observed with trifunctional reactive diluents. Mono functional reactive diluents and pure resins performances are similar and differs from sample to sample.

If the performance of hardener 3 with resin and reactive diluents types are compared, in all resin and reactive diluent types it is observed that the highest pot-lives belongs to the mixtures with 15 % reactive diluent proportions. Also in this table, generally lowest pot-lives are achieved by the difunctional reactive diluent mixtures.

The performance sequence of resin types for pot-life test is also similar with the one for strength tests, that is, Bisphenol F mixtures performs better than Bisphenol A and A/F resins. And generally Bisphenol A performs better than Bisphenol A/F resin. This consideration is also valid for the results of Hardener 6 mixtures. In figure 5.6. figure 5.7. and figure 5.8. pot-life comparisons of samples are seen.

Table 5.4: Pot-life results of the samples with different hardeners and reactive diluents

Mixture	Hardener	Quantity(g)	Pot-life (min.)
Bis A + % 5 RDMF	Hr 2	34	60
Bis A + %10 RDMF	Hr 2	34	111
Bis A + %5 RDTF	Hr 2	34	53
Bis A + %10RDTF	Hr 2	34	59
Bis A + % 5 RDDF	Hr 2	34	46
Bis A + %10 RDDF	Hr 2	34	59
Bis A + % 5 RDMF	Hr 1	40	60
Bis A + %10 RDMF	Hr 1	40	53
Bis A + %5 RDTF	Hr 1	40	46
Bis A + %10RDTF	Hr 1	40	50
Bis A + % 5 RDDF	Hr 1	40	44
Bis A + %10 RDDF	Hr 1	40	44
Bis A + % 5 RDMF	Hr 3	13	53
Bis A + %10 RDMF	Hr 3	13	57
Bis A + %5 RDTF	Hr 3	13	36
Bis A + %10RDTF	Hr 3	13	39
Bis A + % 5 RDDF	Hr 3	13	32
Bis A + %10 RDDF	Hr 3	13	40
Bis A + % 5 RDMF	Hr 5	42,6	111
Bis A + %10 RDMF	Hr 5	42,6	112
Bis A + %5 RDTF	Hr 5	42,6	95
Bis A + %10RDTF	Hr 5	42,6	82
Bis A + % 5 RDDF	Hr 5	42,6	79
Bis A + %10 RDDF	Hr 5	42,6	86
Bis A + % 5 RDMF	Hr 5+10%Act	42,6+10	45
Bis A + %10 RDMF	Hr 5+10%Act	42,6+10	51
Bis A + % 5 RDTF	Hr 5+10%Act	42,6+10	44
Bis A + %10 RDTF	Hr 5+10%Act	42,6+10	41
Bis A + % 5 RDMF	Hr 6	20	59
Bis A + %10 RDMF	Hr 6	20	60
Bis A + %5 RDTF	Hr 6	20	42
Bis A + %10RDTF	Hr 6	20	47
Bis A + % 5 RDDF	Hr 6	20	46
Bis A + %10 RDDF	Hr 6	20	50
Bis A + % 5 RDMF	Hr 4	37,2	210
Bis A + %10 RDMF	Hr 4	37,2	240++
Bis A + %5 RDTF	Hr 4	37,2	240++
Bis A + %10RDTF	Hr 4	37,2	158
Bis A + % 5 RDDF	Hr 4	37,2	175
Bis A + %10 RDDF	Hr 4	37,2	185
Bis A + %10 RDMF	Hr 4+10%Act	37,2+10	240++
Bis A	Hr 4+10%Act	37,2+10	174
Bis A + %10 RDMF	Hr 4+30%Act	37,2+30	60
Bis A	Hr 4+30%Act	37,2+30	50

Table 5.5: Pot-life results of the samples

Resin Mix	Pot life	Resin Mix	Pot life	Resin Mix	Pot life
RFA30+HR 6	40	RFA30 + HR 3	31	RA + HR 2	74
RA+HR 6	57	RA + HR 3	39	RA+RDMF (10%) + HR 2	71
RF+HR 6	34	RF + HR 3	20	RA +RDDF (10%)+ HR 2	93
RFA30 (% 90)+ RDMF(%10) +HR 6	67	RFA30 (% 90)+ RDMF(%10) +HR 3	75	RA+RDTF (10%) + HR 2	59
RFA30 (% 90)+ RDDF(%10) +HR 6	63	RFA30 (% 90)+ RDDF(%10) +HR 3	29	RA + HR 1	40
RFA30 (%90)+RDTF (%10) +HR 6	53	RFA30 (%90)+RDTF (%10) +HR 3	55	RA+RDMF (10%) + HR 1	53
RA (% 90)+ RDMF(%10) +HR 6	60	RA (% 90)+ RDMF(%10) +HR 3	57	RA +RDDF (10%)+ HR 1	86
RA (% 90)+ RDDF(%10)+ HR 6	85	RA (% 90)+ RDDF(%10) +HR 3	40	RA+RDTF (10%) + HR 1	50
RA (%90)+RDTF (%10) + HR 6	47	RA (%90)+RDTF (%10) +HR 3	42	RA + HR 5	114
RF (% 90)+ RDMF(%10) +HR 6	53	RF (% 90)+ RDMF(%10) +HR 3	51	RA+RDTF (10%) + HR 5	82
RF (% 90)+ RDDF(%10) + HR 6	52	RF (% 90)+ RDDF(%10) +HR 3	33	RA+RDMF (10%) +HR 5	112
RF (%90)+RDTF (%10) +HR 6	43	RF (%90)+RDTF (%10) +HR 3	15	RA +HR 5+ 10%Act.	48
RFA(%95)+RDMF (%5) +HR 6	61	RFA30 (%95)+RDMF (%5)+HR 3	60	RA+RDMF(10%)+HR 5+10%Act.	51
RFA(%85)+ RDMF (%15) +HR6	70	RFA(%85)+ RDMF (%15) +HR 3	75	RA+RDTF (10%)+HR 5+10%Act.	41
RA (%95)+RDMF (%5) + HR 6	59	RA (%95)+RDMF (%5) +HR 3	53	RA +HR 4	169
RA(%85)+RDMF (%15) +HR 6	120	RA(%85)+RDMF (%15) +HR 3	83	RA+RDMF (10%)+HR 4	no cure
RF(%95)+RDMF (%5) +HR 6	50	RF(%95)+RDMF (%5) +HR 3	45	RA+RDTF (10%)+HR 4	158
RF(%85)+RDMF (%15)+HR 6	73	RF(%85)+RDMF (%15) +HR 3	64	RA +HR 4+30%Act.	50
RA +RDDF (10%)+ HR 5	175	RA + RDDF (10%) +HR 4	no cure	RA+RDMF(10%)+HR 4+30%Act.	60
RA+RDDF (10%)+ HR 5+ 10% Act.	63	RA+RDDF(10%) +HR 4+30% Act.	57	RA+RDTF (10%)+HR 4+30%Act.	70

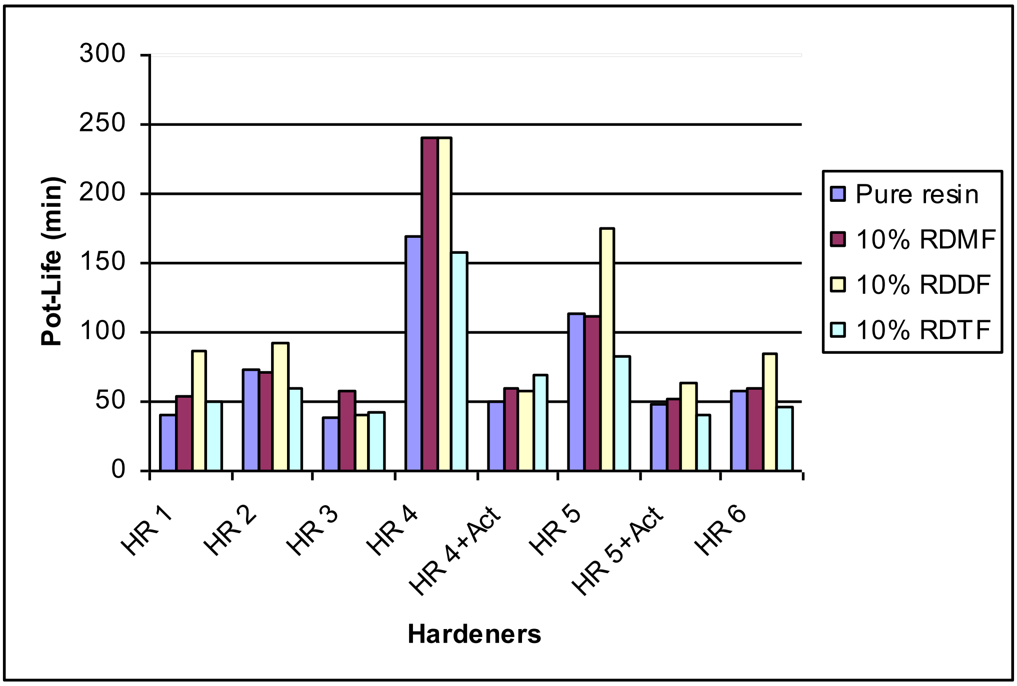


Figure 5.8: Pot-life comparison between hardener types for bisphenol A resin with different reactive diluent additions

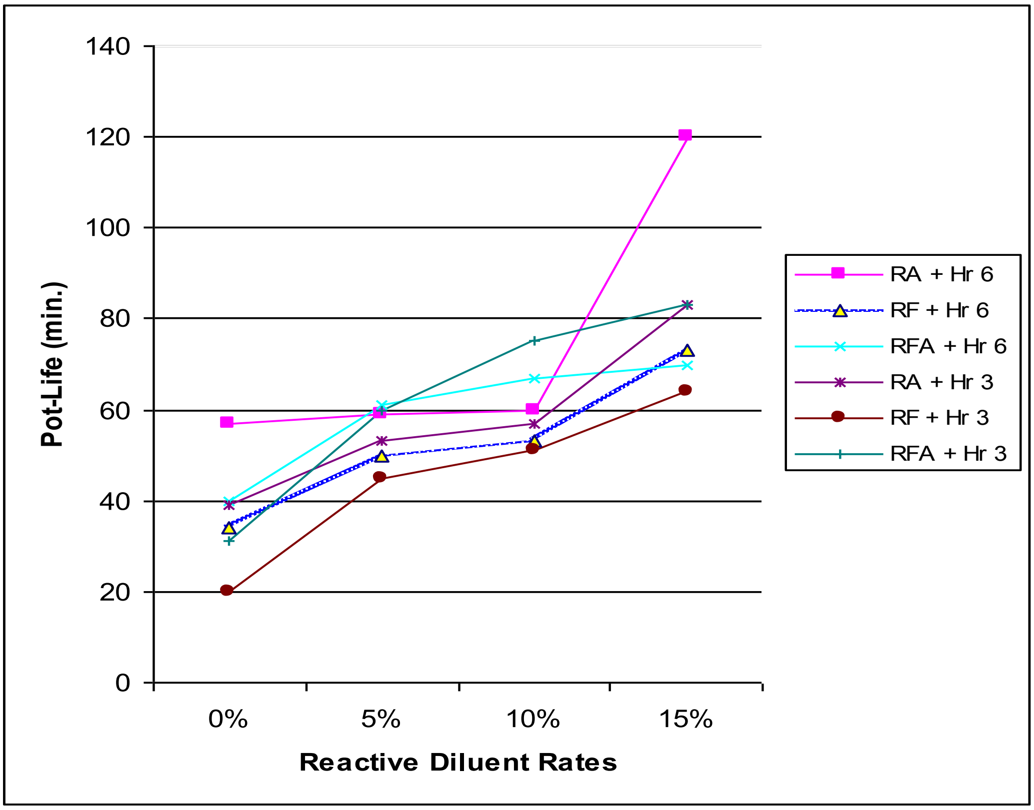


Figure 5.9: Pot-life comparison of different resin mixtures with addition of various rates of reactive diluents

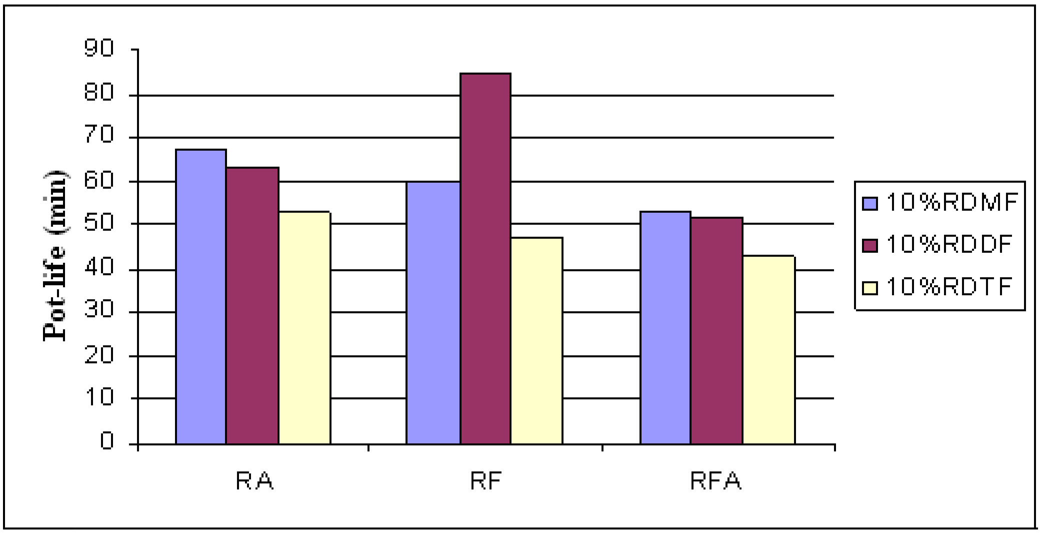


Figure 5.10: Pot-life comparison for hardener 6 mixtures with different resin types.

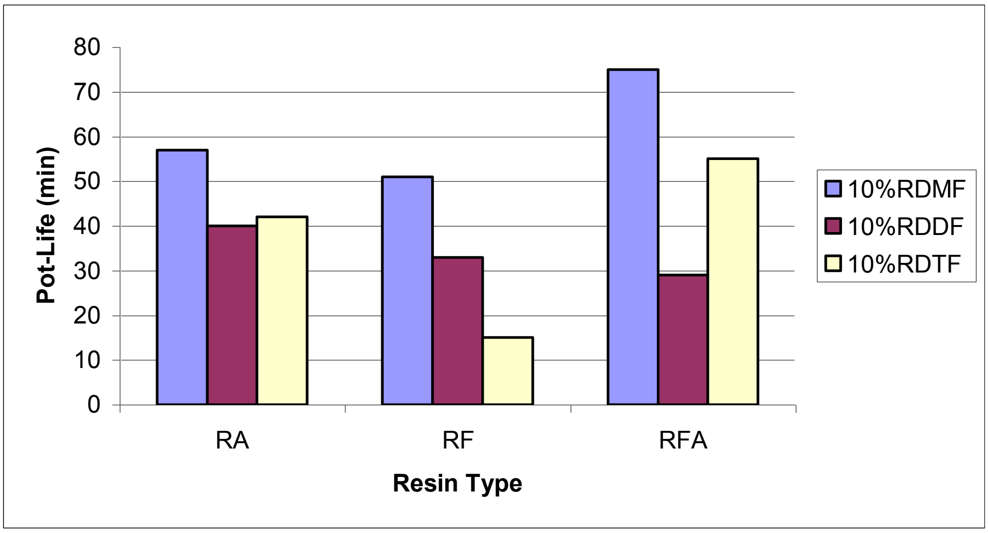


Figure 5.11: Pot-life comparison for hardener 3 mixtures with different resin types.

5.3 Hardened State Measurements

5.3.1 Bending and Compressive Strength

This tests are applied to a great number of samples to provide comparing the affects of reactive diluents, hardeners and resin types over strength.

These evaluations are made by considering both one day and 14 day results since they are generally similar.

The mixtures which gives the best results are same while the minimum results differ in each group. The best result is provided by the mixture RFA30 and 10% difunctional reactive diluent with hardener 3 (TETA) and hardener 6 (tertiary amine).

When the hardeners performances are compared it is seen that the best results are given by hardener 3.

According to the pot-life test results, for accelerating the pot-life 30 % activator (benzyl alcohol) is added to mixtures with hardener 4 and strength test are applied to both activated and normal mixtures. The activator amount is again determined stoichiometrically.

Results showed that unactivated mixtures has the best results after hardener 3, while the mixtures with activator shows the worst performance, even some mixtures of that group hadn’t been solidified in one day for one day tests. Solidified samples were also very flexible, showed plastic like behaviour and could be bended with hand. Activator addition decreased the results in large amounts, at least 80 %.

In hardener 5 case, results was opposite of the case of hardener 4. Activator amount was10 % for hardener 5, addition of 10 % activator increases the results slightly and this mixtures exhibit strengths closer to average values. However, the samples of hardener 5 showed the lowest strength results if we compare them with the results of other specimen without activator.

The sequence of hardeners without activator addition, from the best performing to the worst performing is;

Hardener 3 > Hardener 4 > Hardener 1 > Hardener 2 > Hardener 6 > Hardener 5

It is seen that the performances of hardener 2 and hardener 1 are also good. But the results of hardener 6 is not acceptable, it gives also flexible samples.

The sequence changes so with activator added situation;

Hr 3 > Hr 4 > Hr 1 > Hr 2 > Hr 5+10% Act .> Hr 6 >Hr 5 > Hr 4+30% Act.

If the reactive diluents performances are compared, with mentioning that it may differ generally difunctional reactive diluent gave better results than monofunctional and trifunctional reactive diluents. Although for same mixtures trifunctional reactive diluent gave better results than difunctional reactive diluent mixtures but majority belonged to difunctional mixtures. So it is obvious that monofunctional reactive diluents gave lower results.

For comparing the resins, although the results are not very distinctive, RFA30 and RF resins showed generally better results than resin RA.

According to the results of this test, the samples for chemical resistance and adhesion tests were determined. Table 5.6. shows the one day strength results and table 5.7. shows the results for 14 days. Figure 5.9, 1 day bending results of samples with different hardener and reactive diluent types.

Following tables are given in Appendixes part.

Table 5.6: Bending and compressive strength results for 1 day samples

Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)	Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)
RFA30+HR 6	8,25	30,19	RFA30 + HR 3	24,59	83,73
RA+HR 6	7,9	41,59	RA + HR 3	18,53	75,94
RF+HR 6	8,32	40,46	RF + HR 3	25,95	79,74
RFA30 (% 90)+ RDMF(%10) +HR 6	7,75	32,25	RFA30 (% 90)+ RDMF(%10) +HR 3	19,64	46,38
RFA30 (% 90)+ RDDF(%10) +HR 6	8,43	39,6	RFA30 (% 90)+ RDDF(%10) +HR 3	26,95	89,18
RFA30 (%90)+RDTF (%10) +HR 6	8,17	42	RFA30 (%90)+RDTF (%10) +HR 3	25,96	71,75
RA (% 90)+ RDMF(%10) +HR 6	7,49	38,85	RA (% 90)+ RDMF(%10) +HR 3	22,9	59,99
RA (% 90)+ RDDF(%10)+ HR 6	8,31	41,65	RA (% 90)+ RDDF(%10) +HR 3	25,29	80,03
RA (%90)+RDTF (%10) + HR 6	6,67	40,26	RA (%90)+RDTF (%10) +HR 3	30,48	87,92
RF (% 90)+ RDMF(%10) +HR 6	9,12	45,37	RF (% 90)+ RDMF(%10) +HR 3	22,65	49,15
RF (% 90)+ RDDF(%10) + HR 6	9,22	44,1	RF (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RF (%90)+RDTF (%10) +HR 6	8,69	46,98	RF (%90)+RDTF (%10) +HR 3	27,64	71,64
RFA(%95)+RDMF (%5) +HR 6	7,93	37,41	RFA30 (%95)+RDMF (%5)+HR 3	25,96	80,89
RFA(%85)+ RDMF (%15) +HR6	7,8	38,5	RFA(%85)+ RDMF (%15) +HR 3	19,42	44,37
RA (%95)+RDMF (%5) + HR 6	7,01	35,47	RA (%95)+RDMF (%5) +HR 3	24,11	81,87
RA(%85)+RDMF (%15) +HR 6	6,49	37,48	RA(%85)+RDMF (%15) +HR 3	20,72	50
RF(%95)+RDMF (%5) +HR 6	8,37	41,1	RF(%95)+RDMF (%5) +HR 3	19,4	41,3
RF(%85)+RDMF (%15)+HR 6	8,52	39,66	RF(%85)+RDMF (%15) +HR 3	27,67	77,88
RA + HR 2	12,49	75,17	RA + HR 5	4,5	26,39
RA+RDMF (10%) + HR 2	22,06	63,84	RA+RDTF (10%) + HR 5	5,49	33,32
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	20,26	83,03	RA+RDMF (10%) +HR 5	5,32	28,13
RA + HR 1	10,05	40,10	RA +HR 5+ 10%Act.	7,81	44,2
RA+RDMF (10%) + HR 1	22,1	44,17	RA+RDMF(10%)+HR 5+10%Act.	19,22	53,07
RA +RDDF (10%)+ HR 1	24,97	56,63	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	20,11	46,06	RA+RDTF (10%)+HR 5+10%Act.	23,66	68,92
RA (100) +HR 4	22,25	39,63	RA (100)+ HR 4+ 30% Act.	6,12	10,43
RA+RDMF (10%)+HR 4	23,22	42,36	RA+RDMF (10%)+ HR 4+ 30% Act.	1,71	2,76
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	25,72	54,12	RA+RDTF (10%)+ HR 4+ 30% Act.	3,79	6,35

Note: The grey cells show two day strength results.

Table 5.7: Bending and compressive strength results for 14 day of samples

Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)	Resin Mix	Bending Str. (N/mm2)	Compr. Str. (N/mm2)
RFA30+HR 6	10,64	56,57	RFA30 + HR 3	26,38	97,00
RA+HR 6	6,4	41,24	RA + HR 3	26,71	97,21
RF+HR 6	10,83	58,55	RF + HR 3	26,89	93,08
RFA30 (% 90)+ RDMF(%10) +HR 6	12,96	68,6	RFA30 (% 90)+ RDMF(%10) +HR 3	23,69	78,18
RFA30 (% 90)+ RDDF(%10) +HR 6	13,32	67,57	RFA30 (% 90)+ RDDF(%10) +HR 3	30,69	103,73
RFA30 (%90)+RDTF (%10) +HR 6	9,71	51,54	RFA30 (%90)+RDTF (%10) +HR 3	29,33	90,87
RA (% 90)+ RDMF(%10) +HR 6	9.68	57,31	RA (% 90)+ RDMF(%10) +HR 3	23,33	62,74
RA (% 90)+ RDDF(%10)+ HR 6	8,82	43,69	RA (% 90)+ RDDF(%10) +HR 3	28,05	97,77
RA (%90)+RDTF (%10) + HR 6	9,43	48,54	RA (%90)+RDTF (%10) +HR 3	28,04	98,34
RF (% 90)+ RDMF(%10) +HR 6	12,04	64,63	RF (% 90)+ RDMF(%10) +HR 3	20,99	58,76
RF (% 90)+ RDDF(%10) + HR 6	14,22	78,86	RF (% 90)+ RDDF(%10) +HR 3	29,14	95,24
RF (%90)+RDTF (%10) +HR 6	12,2	71,85	RF (%90)+RDTF (%10) +HR 3	27,82	76,42
RFA(%95)+RDMF (%5) +HR 6	10,68	52,53	RFA30 (%95)+RDMF (%5)+HR 3	23,76	71,99
RFA(%85)+ RDMF (%15) +HR6	12,72	60,15	RFA(%85)+ RDMF (%15) +HR 3	21,69	58,27
RA (%95)+RDMF (%5) + HR 6	9,3	47,87	RA (%95)+RDMF (%5) +HR 3	23,3	74,05
RA(%85)+RDMF (%15) +HR 6	12,24	63,87	RA(%85)+RDMF (%15) +HR 3	19,29	56,12
RF(%95)+RDMF (%5) +HR 6	14,91	73,18	RF(%95)+RDMF (%5) +HR 3	22,7	62,2
RF(%85)+RDMF (%15)+HR 6	19,78	80,77	RF(%85)+RDMF (%15) +HR 3	19,48	48,79
RA + HR 2	16,07	82,01	RA + HR 5	5,62	32,25
RA+RDMF (10%) + HR 2	18,08	58,16	RA+RDTF (10%) + HR 5	6,02	35,18
RA +RDDF (10%)+ HR 2	28,93	80,38	RA +RDDF (10%)+ HR 5	4,92	27,43
RA+RDTF (10%) + HR 2	23,36	77,78	RA+RDMF (10%) +HR 5	6,18	30,69
RA + HR 1	17,77	43,46	RA +HR 5+ 10%Act.	9,58	45,62
RA+RDMF (10%) + HR 1	19,21	41,43	RA+RDMF(10%)+HR 5+10%Act.	10,35	47,26
RA +RDDF (10%)+ HR 1	24,97	56,93	RA+RDDF (10%)+ HR 5+ 10% Act.	18,96	48,36
RA+RDTF (10%) + HR 1	22,04	47,21	RA+RDTF (10%)+HR 5+10%Act.	19,57	49,88
RA (100) +HR 4	24,17	53,68	RA (100)+ HR 4+ 30% Act.	5,36	7,54
RA+RDMF (10%)+HR 4	25,03	54,98	RA+RDMF (10%)+ HR 4+ 30% Act.	3,49	6,5
RA+RDDF (10%) +HR 4	24,27	50,59	RA+RDDF (10%) + HR 4+ 30% Act.	4,13	7,82
RA+RDTF (10%) +HR4	26,88	64,25	RA+RDTF (10%)+ HR 4+ 30% Act.	5,69	8,76

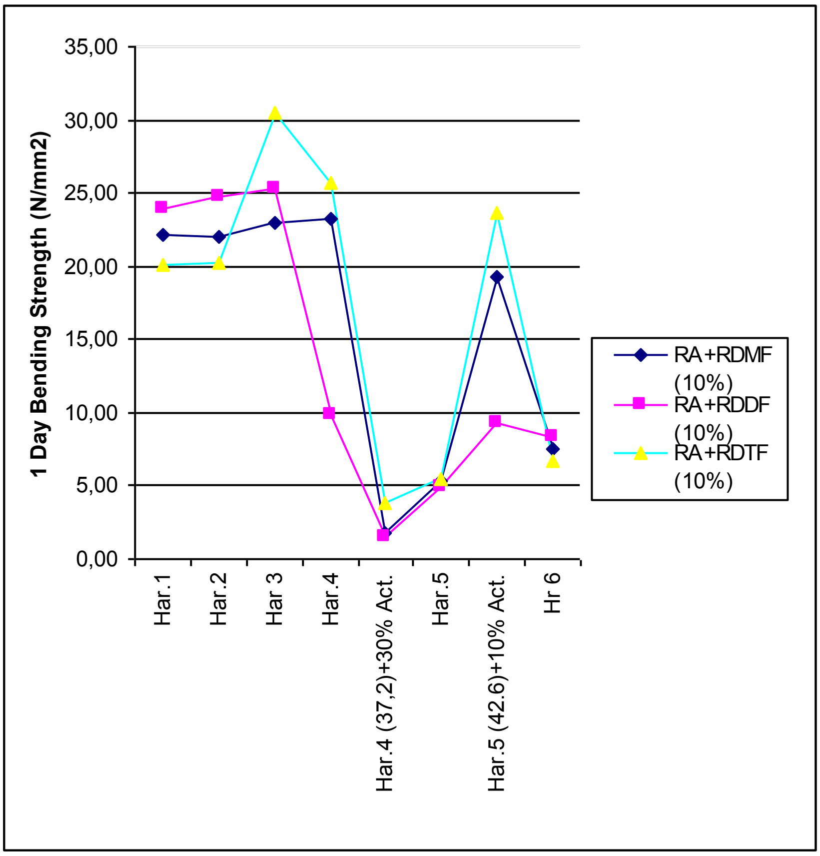


Figure 5.12: 1 day bending results of samples with different hardener and reactive diluent types.

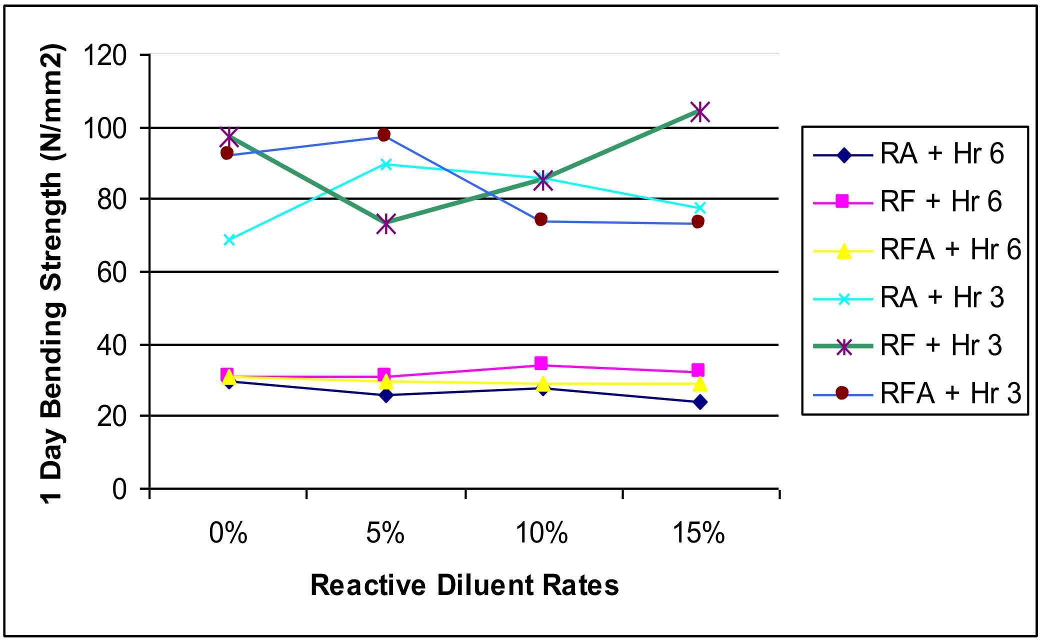


Figure 5.13: 1 day bending test results of resins with Hr 3 and Hr 6.

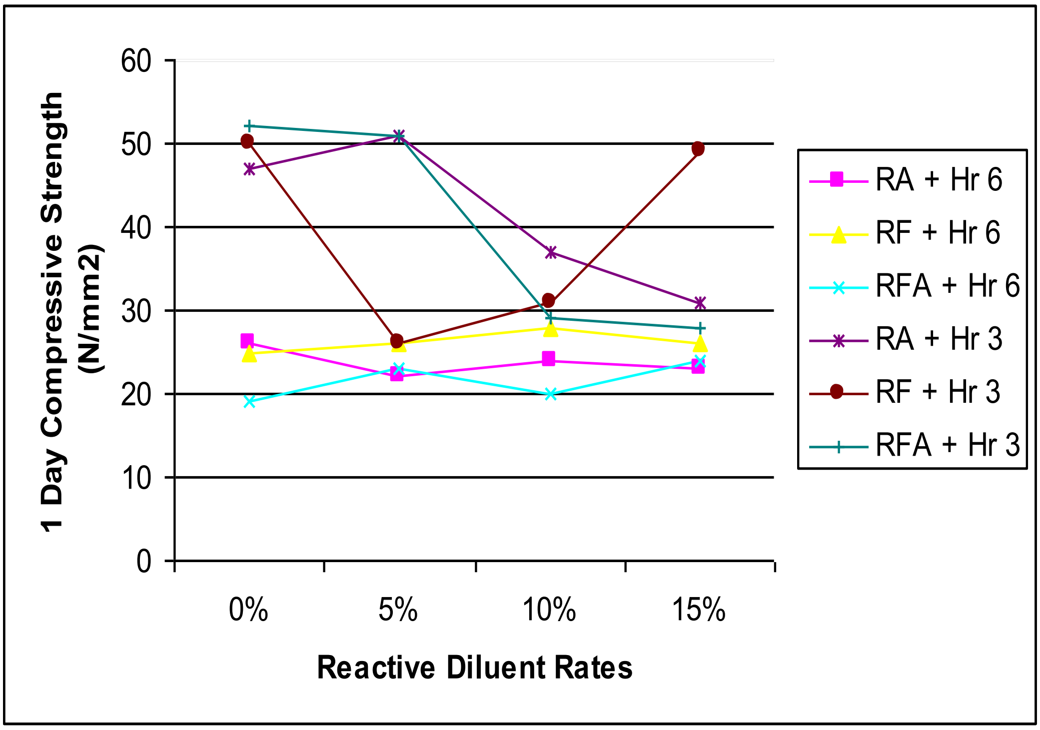


Figure 5.14: 1 day compression test results of resins with Hr 3 and Hr 6.

Also cure temperature is very important, curing at elevated temperature increases the mechanical strength because it decreases the number of unreacted amine groups, which means higher degree of cross-linking. In this study, samples were cured at room temperature but if they would be cured at higher temperatures more strength would be gained.

5.3.2 Durability-Chemical Resistance

For the chemical resistance test, most effective solutions over epoxy were chosen, these are alcohol, 37 % formaldehyde, 15 % lactic acid and 20 % formic acid.

15 samples were chosen for comparing the performances of resins, hardeners and for considering the effects of reactive diluent addition on chemical resistance with different rates and different functionalities.

For a general evaluation, while the resistance of samples to formaldehyde and alcohol are good, most of them completed the 3 weeks of test time with no damage, but on the other hand no sample left undamaged towards the 15% lactic acid and 20% formic acid solutions. The level of the damage was changed according to the performances of samples. Chemical resistance test results are given on table 5.8.

Following table shows the results of chemical resistance test. The meanings of the letters used on table are ;

A	No damage
B	Low damage
C	Moderately damaged
D	Colour fading
E	Hardly damaged

Table 5.8: Results of chemical resistance test

No.	Chem.	1.week	2.week	3.week	1.week	2.week	3.week	Chem.	No.
1	Formald.	A	A	B	A	A	A	Formald.	9
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	E	E	C	C	C	Formic A	
	Lactic A	C	C	E	C	C	C	Lactic A	
2	Formald.	A	A	A	A	A	A	Formald.	10
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	E	E	C	C	E	Formic A	
	Lactic A	C	C	E	C	C	C	Lactic A	
3	Formald.	A	A	A	A	A	A	Formald.	11
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	B	C	C	C	E	E	Formic A	
	Lactic A	B	C	C	C	C	E	Lactic A	
4	Formald.	A	A	A	A	A	A	Formald.	12
	Alcohol	A	A	A	A	A	B	Alcohol	
	Formic A	A	C	C	E	E	E	Formic A	
	Lactic A	B	C	C	E	E	E	Lactic A	
5	Formald.	A	A	A	A	A	A	Formald.	13
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	C	C	C	C	C	C	Formic A	
	Lactic A	B	B	C	C	E	E	Lactic A	
6	Formald.	A	A	A	A	A	A	Formald.	14
	Alcohol	A	A	A	A	B	B	Alcohol	
	Formic A	E	E	E	C	E	E	Formic A	
	Lactic A	C	E	E	E	E	E	Lactic A	
7	Formald.	A	A	A	A	A	A	Formald.	15
	Alcohol	A	A	A	A	A	A	Alcohol	
	Formic A	A	B	B	C	E	E	Formic A	
	Lactic A	A	B	B	B	E	E	Lactic A	
8	Formald.	A	A	A	A	A	A	Formald.	R
	Alcohol	A	A	B	A	A	A	Alcohol	
	Formic A	E	E	E	B	C	C	Formic A	
	Lactic A	E	E	E	B	C	C	Lactic A	

R means reference in this table. Reference mixture is “RA + Hr 3” which is same with sample 3. Final results will show the reliability of this tests. Environmental conditions are very important.

For comparing the resin performance, results of the mixtures including bisphenol A, bisphenol F and bisphenol A/F resins with Hr.3 addition were observed. This observation revealed that the performance of bisphenol A is much better than the one for bisphenol F and bisphenol A/F. Bisphenol F and bisphenol A/F has the same resistance nearly, they are damaged greatly by formic and lactic acid solutions, but bisphenol F is also unresistant to formaldehyde even its damage is very slight. It is the only mixture which was damaged by formaldehyde.

In this experiment five hardeners are used, the unused hardener was Hr.6, tertiary amine, which is said to be chemically unresistant. Resin mixtures were including bisphenol A resin and hardeners respectively Results showed that Hr.3, TETA, and Hr.1, TMD, performs better, but the mixture with Hr.3 started to decaying 1 week later than the mixture with Hr.1 for lactic and formic acid solutions. Hr.2, also showed the same result with Hr.1, but it was damaged greater than Hr.1 mixture in formic acid. The performance of the mixture with Hr.4. performed worse than these mixtures, whose results are among the bad results in the table. The worst performance is the one for the mixture with Hr.5, there are samples which has same results with Hr.5 after 3 weeks time but it started decaying more quick than them. It was also damaged by alcohol unlike most of the samples.

If the performance of Hr.5 is compared with its activator added state, as it was seen in compressive and bending tests, an increase in performance was observed. This was especially valid for formic acid, “moderate damage” took place of “great damage”. Also no damage was observed for activator added sample in alcohol unlike other one.

Effect of reactive diluent addition was also evaluated with mixtures including reactive diluent with the rates of 5 %, 10 %, %15 and the mixture which doesn’t include reactive diluent. This comparison was made with monofunctional reactive diluent. The included hardener was Hr.3. It was seen that performance increases with decreasing amount of reactive diluent. This was a parallel result with compressive and bending tests results. Performances of 5 % reactive diluent added mixture and the mixture with no reactive diluent were similar, but 5 % reactive diluent added mixture was performed better in lactic acid.

The functionality of reactive diluents affect also performance, the mixture with trifunctional reactive diluent performed best, it was slightly damaged by formic acid and lactic acid. This mixture with Hr.3 had the best performance among all. The effect of reactive diluent comparison was made also with trifunctional diluent with 5% and 10% rates. But on the contrary of the results observed for monofunctional diluent, 10% trifunctional reactive diluent added sample performed much better than 5% reactive diluent added sample. This may be because the performance increasing effect of trifunctional reactive diluent. The mixture with monofunctional reactive diluent followed it but the one with difunctional reactive diluent performed worse than this two. The rate of reactive diluents in this mixtures was 10%.

A mixture of bisphenol A resin and 10 % difunctional reactive diluent addition are tried with both Hr.3 and Hr.5 addition. Results was similar but the mixture with Hr.3 performed better. But that showed that difunctional reactive diluent addition affects the performance badly, since the mixture with Hr.3 showed very well results with other additions .

5.4 Pull-off Adhesion Test

The presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives . The resins cure with low shrinkage, so that the various surface contacts set up between the resin and adherent [14].

The excellent adhesive properties exhibited by epoxies is due in large part to pendent hydroxyl groups which exist within the molecular structures of most epoxies and which are considered capable of interacting, via hydrogen bond formation [7].

Adhesive forces may be expected to arise from Van Der Waals interactions between absorbent and absorbate [14].

Breaking plane was concrete or epoxy mortar planes for the samples with high bonding strength while it was adhesion plane for the mixes with low bonding strength. The results of pull-off test are shown on table 5.9. The meanings of the letters are given in chapter 4, in 4.5.3. pull-off adhesion test section.

Table 5.9 : Pull-off test results showing the adhesion strength f_h values and fracture surface of the samples.

Sample	1. value (MPa)	2.value (MPa)	3. value (MPa)	f_h (MPa)
RF + Hr.3. + Sand	5,12	4,64	4,40	4,72
Fracture surface	A	-/Y	-/Y	
RFA30 + Hr.3.+ Sand	4,70	5,06	4,34	4,70
Fracture surface	-/Y	A	-/Y	
RA +Hr.3 + Sand	8,52	9,12	-	8,82
Fracture surface	A	A	A	
RA (%95) + RDMF (%5)+ Hr.3 + Sand	4,17	3,20	3,60	3,66
Fracture surface	-/Y	Y	Y	
RA (%90) + RDMF (%10)+ Hr.3 + Sand	3,42	2,17	2,45	2,68
Fracture surface	-/Y	Y	Y	
RA (%90) + RDDF (%10)+ Hr.3 + Sand	5,02	3,58	5,86	4,82
Fracture surface	-/Y	Y	A	
RA (%90) + RDTF (%10)+ Hr.3 + Sand	4,96	4,42	4,66	4,68
Fracture surface	-/Y	-/Y	-/Y	
RA (%85) + RDMF (%15)+ Hr.3 + Sand	2,78	3,74	3,56	3,36
Fracture surface	Y	-/Y	-/Y	
RA + Hr.1 + Sand	5,64	3,40	5,09	4,71
Fracture surface	A	-/Y	-/Y	
RA + Hr.2 + Sand	14,6	13,8	-	14,2
Fracture surface	A	A	A	
RA + Hr.4 + Sand	2,96	4,02	4,27	3,75
Fracture surface	-/Y	B	B	
RA +Hr.5 + Sand	2,02	1,96	3,64	2,54
Fracture surface	Y	Y	A/B	
RA + Hr.5 + % 10 Activator + Sand	10,16	8,76	-	9,46
Fracture surface	A	A	A	
RA (%90) + RDDF (%10)+ Hr.5 + Sand	5,80	4,22	3,24	4,42
Fracture surface	A	A/B	Y	
RA (%95) + RDTF (%5)+ Hr. 3 + Sand	6,70	5,45	3,45	5,20
Fracture surface	A	A/B	-/Y	

Performance sequence of hardeners are seen below;

Hr 2 >Hr 5+10% Activator > Hr 3 > Hr 1 > Hr 4 > Hr 5

Hardener 2 is the best performing sample as expected because it was mentioned that it provides excellent adhesion. Also the performance of hardener 3 was good, although it is an effective cross-linker .

Hardener 5 showed the worst performance for the mixtures including bis A resin. 10% activator addition increased the performance prominently, and makes this mixture second best performing. But unactivated sample of hardener 5 was the worst performing. Also hardener 4 performed bad. Hardener performances was parallel with other tests.

Figure 5.10 shows the adhesion strength comparisons according to hardener type used.

Resin performances were evaluated with the mixtures including hardener 3. Test showed that bis A resin performed better than bis F and bis A/F resins. But the performances of bis F and bis A/F were same.

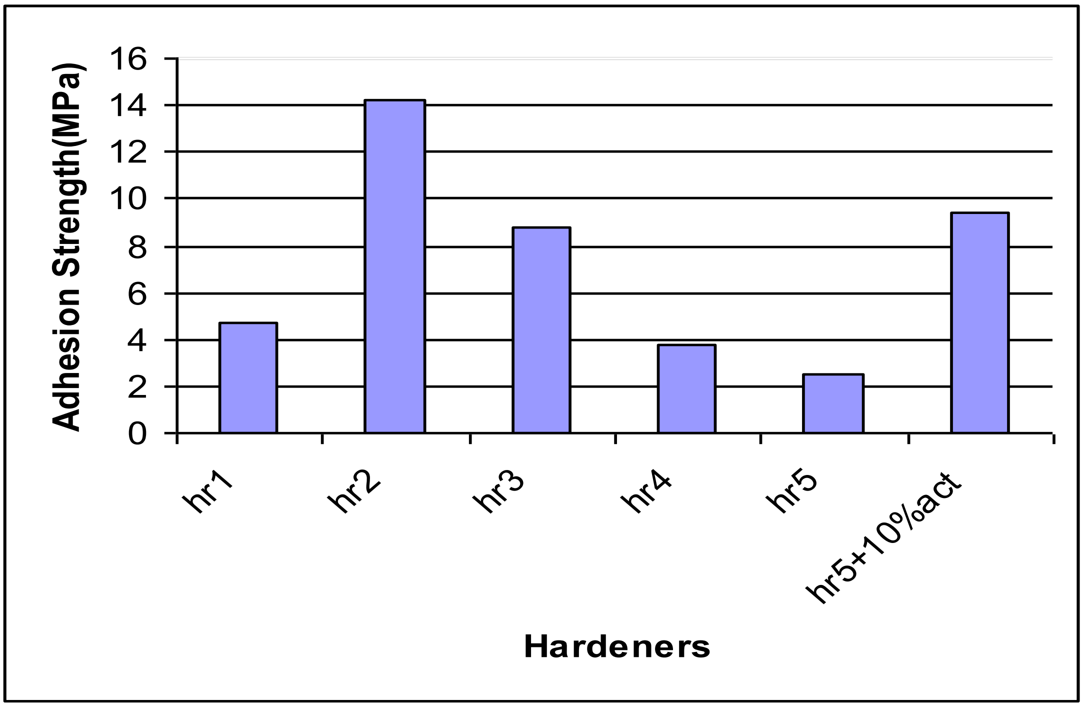


Figure 5.15 : Adhesion strength comparison according to hardener type used.

For considering reactive diluent functionality effects, difunctional reactive diluent performed best, then trifunctional reactive diluent comes whose results was similar with difunctional one and the worst performing one is monofunctional in 10% of reactive diluent added samples. Performance decreasing effects of reactive diluents was observed here as the pure resin performance of bis A with hardener 3 was very high, this effect was mostly seen for monofunctional reactive diluent. Figure 5.11 shows the performances of mixtures including hardener 3.

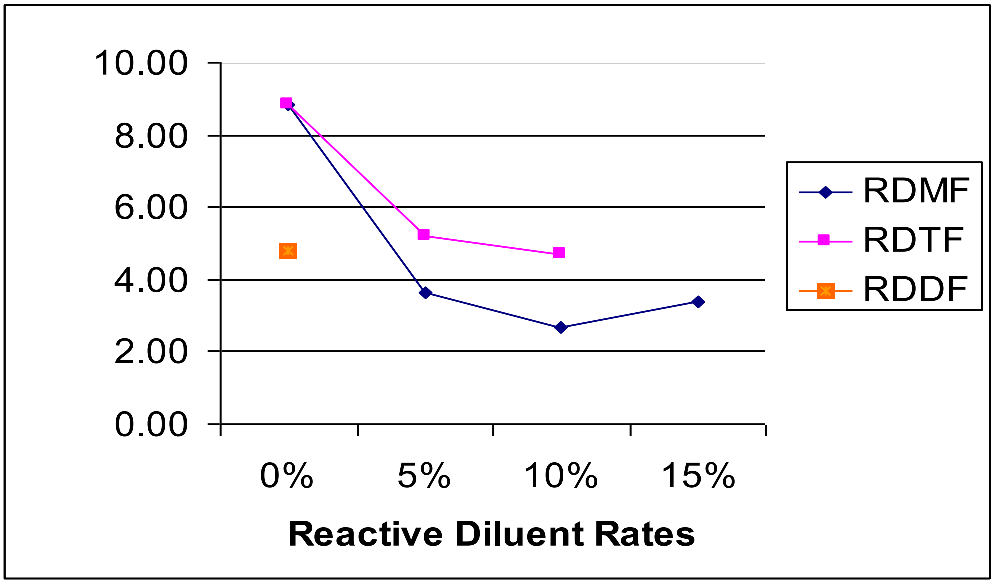


Figure 5.16 : Adhesion strength change with various rates of reactive diluent addition.

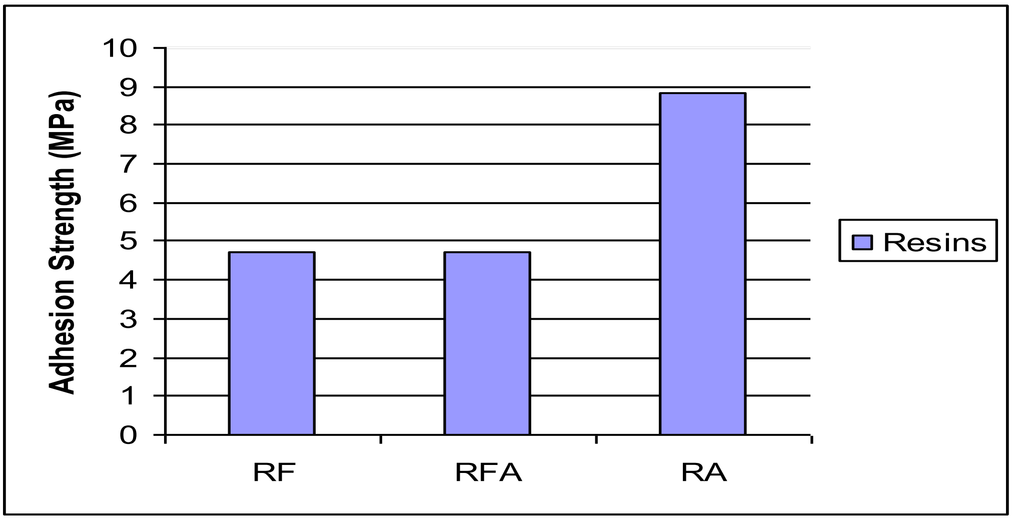


Figure 5.17 : Effect of diluent type on adhesion strength of resin A and hardener 3.

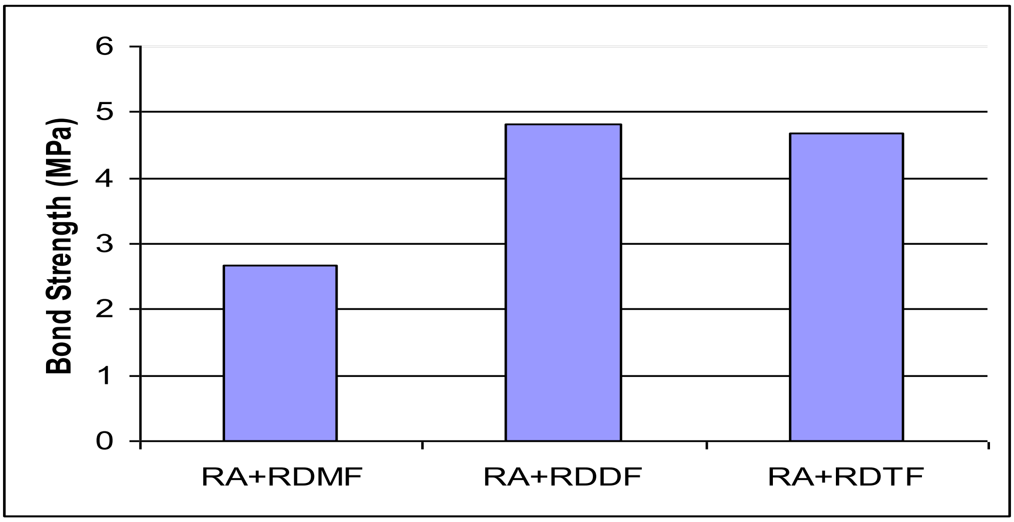


Figure 5.18 : Performances of mixtures including hardener 3.

Reactive diluent addition was lowered the results. For monofunctional reactive diluent, the highest value was reached with the lowest reactive diluent ratio. But unexpectedly the results of 15% monofunctional reactive diluent added sample performed slightly better then 10% of monofunctional reactive diluent added sample. Even 5% reactive diluent addition decreases the adhesion strength in huge amounts.

Also for trifunctional reactive diluent, 5% trifunctional added sample performed better than 10% trifunctional reactive diluent added sample as expected.

Difunctional reactive diluent was tried both with hardener 3 and hardener 5. Results was similar as in chemical resistance test. This shows that difunctional reactive diluent has an important effect on results.

6. CONCLUSION

In this chapter a general evaluation of the study and experiments were done.

6.1 Conclusions On Rheological Properties

6.1.1 Viscosity and Flow–table

Since flow-table results are dependent on viscosity, it would be proper to examine them together.

As the experiments show, pure viscosity of resins decreases as the reactive diluent addition, decreased viscosities are harmonious with the first values. Pure bisphenol A resin has the highest viscosity and bisphenol F has the lowest in pure resins, and the mixture of this two resin bisphenol A/F has a viscosity between them. As it is mentioned previously chemical constitution of epoxy resin affects the viscosity. Cycloaliphatic ones will have higher viscosities than linear aliphatics. Bisphenol A molecules are bigger than the mentioned resin molecules.

6.2 Pot-life

The results of this test for the samples for comparing pot-life times according to hardener types with out any activator addition was like below;

Hardener 3 < Hardener 1 < Hardener 6 < Hardener 2 < Hardener 5 < Hardener 4.

According to this sequence Hardener 3 (TETA) performs best. It gave a pot-life less than 1 hour if stoichiometrical quantities are used.

TETA is a highly reactive curing agent and it has a short chain length, also its molecular weight is low, these properties provides a short pot-life.

Hardener 1 (TMD) also performs good in pot-life tests. Although it has a longer chain than TETA, this length is accepted moderate. Also its high reactivity causes a good pot-life performance.

Hardener 6 (tertiary amine) is accepted as providing an optimum cure rate which is not short nor long that gives opportunity for some modifications before complete cure occurs. It is not much reactive.

Hardener 2 gives longer pot-lives although it is accepted as having high reactivity, this performance may be considered as a consequence of the rigid nature of the non-conjugated aromatic ring backbone.

Hardener 5 shares the worst results with hardener 4. This may be because of the cyclohexane rings substituted which increases the size of amine for hardener 5. Hardener 4 has a similar structure with hardener 5 as both having isophorane chemistry. Also it has lower reactivity than other amines and long pot-life time is a characteristic of this curing agent.

Performance sequence for activators added situation is ;

Hr 3 < Hr 1< Hr 5 +% 10 Act.< Hr 6 < Hr 4 + 30 % Act.< Hr 2 <Hr 5 < Hr 4 .

The used activator is benzyl alcohol and it changed the performance of hardener 4 greatly while it did not affect much the one for hardener 5. The quantities of used activator was determined by previous experiences and tries. It is seen that the application areas for hardener 4 and hardener 5 are more appropriate for the ones requiring long pot-lives, it would be a wrong choice to use them for an application requiring short pot-life .

For comparing the used reactive diluent quantities which are 5%, 10% and 15%, 15% performs worst among them, cure time also would depend on the initial viscosity and very viscous, wetty samples would cause a delay in pot-life times.

Functionalities of the reactive diluents also affects the pot-life results. Lowest pot-lives are achieved by difunctional reactive diluent while the highest pot-lives are observed with trifunctional reactive diluents but mono functional reactive diluents and pure resins performances are similar and differs from sample to sample.

On the contrary of monofunctional reactive diluent samples, increase in reactive diluent addition rate also increased the performance for trifunctional reactive diluents when comparing the 5% and 10% additions which was resulted from the performance increasing effect of trifunctional reactive diluent.

For resin types comparing, bisphenol F performs best, then majorly comes bisphenol A/F and then bisphenol A comes. This maybe because of the structure of bisphenol F which is more tend to crystallize and proper for easier cross-linking, and obviously bisphenol A/F resin would perform similar due to its bisphenol F content.

As this experiment shows chain distance of hardener molecule, molecular weight ad reactivity are important parameters for pot-life. So, short chain distance, low molecular weight and high reactivity of hardener would provide shorter pot-lives. For resin considerations more ordered structures would cause easier cross-linking so the shorter pot-lives.

6.3 Conclusions for Hardened State Measurements

6.3.1 Bending (flexural) and Compressive Strength

Bending and compressive strength tests were made both for 1 day and 14 day. These two results showed parallel behaviour. Firstly the pure resin and resins without reactive diluent addition, performances were compared. RF showed the best results, then comes RFA30 and finally RA. This may be because of the more crystalline structure of RF and RFA30 which contains 30% RF resin.

Then the performances of hardeners were compared. Most effective properties of hardeners is reactivity which means the cross-linking property. Because mechanical strength is majorly dependent on cross-linking density of the specimen. Performance sequences are shown below;

Hardener 3 > Hardener 4 > Hardener 1 > Hardener 2 > Hardener 6 > Hardener 5

Hr 3 > Hr 4 > Hr 1 > Hr 2 > Hr 5+10% Act .> Hr 6 >Hr 5 > Hr 4+30% Act.

Hardener 3 is a highly reactive curing agent which also provides the best mechanical strength results. Also hardener 1 and hardener 2 were defined as highly reactive in their data sheets which also have good results proving this information. Hardener 4 while it was mentioned to have lower reactivity in its data sheet, showed good mechanical results. This may be because of the exact stoichiometric quantity it was used and other optimum conditions. But the addition of 30% benzyl alcohol made this mixture worst of this study. The samples with hardener 4 and 30% benzyl alcohol was very ductile, as it is seen in figure 6.1., this picture was taken after compression test. On the other hand 10% addition of benzyl alcohol greatly increased the performance of hardener 5. This reveals the importance of usage quantity. Benzyl alcohol is a general solvent of epoxy resins. Some usage of it may increase the viscosity and may provide better mixing, and this would increase the effect of hardener but on the other hand excess usage of it would obviously decrease the cross-linking density so this would cause a decrease in mechanical properties. Hardener 6 was mentioned as providing high mechanical properties, but it showed bad performance. The samples with hardener 6 was also very ductile. Although the used quantity was determined by stoichiometric calculations, the ratio was nearly 20% of the resin, but in data sheet it was mentioned that if used over 5% of the resin it may decrease some properties. This results may be because of that reason.

Figure 6.1: Sample including hardener 4 and 30% benzyl alcohol ,after compression.

As a general evaluation, reactive diluent added samples were performed better than pure resins. Among reactive diluent added samples, generally difunctional reactive diluent added samples and for some samples trifunctional reactive diluent samples performs better than monofunctional reactive diluent added samples. It was mentioned that polyfunctional reactive diluents may increase some mechanical properties while monofunctional reactive diluents decreases the performances.

As many of the other properties, mechanical properties are mostly dependent on the degree of network structure.

The used hardener quantity is critical and affects the mechanical properties, it is very important to use them in stoichiometric quantities and maybe some lower than this ratio to prevent some amine groups to left unreacted.

6.3.2 Durability-Chemical Resistance

Generally epoxy resins have good chemical resistance due to their chemical structure. It is due to the properties of carbon-amine nitrogen link which is fairly stable in the presence of most inorganic acids, poor in organic acids and good in caustics [15]. According to test results the best performing resin towards the used chemicals is bisphenol A, then comes bisphenol F and bisphenol A/F together whose resistances are nearly same. But Bisphenol F was damaged slightly because of formaldehyde after 3 weeks time, because it also includes formaldehyde. The solvent is told to be a good solvent for a material if it includes the similar molecular structure. If this situation exists, the adhesive forces between the solvent and the polymer are similar to the cohesive forces that exist between solvent molecules or between polymer molecules. The criterion here is “like dissolves like” [35].

Bisphenol A is more resistant than other resins since it includes methylene groups rather than H which would provide more strength structure.

For comparing the hardener performance previously used hardeners except hardener 6, used again, because it was mentioned to be chemically unresistant in its data sheet. Hardener 3 has the best performance especially for formic acid and lactic acid. Its shelf life is longer than other hardeners also which may show its resistance to environmental conditions. As being a relatively small molecule TETA wouldn’t have steric hindrances so it would provide high cross-link densities which is responsible from high chemical resistance. The performances of hardener 3 and hardener 1 are similar but hardener 3 performs better for lactic and formic acids. Hardener 1 has good chemical resistance as it is written in technical data sheet.

Hardener 2 has a moderate chemical resistance which is highly basic. Hardener 4 and hardener 5 has worse performances than others. Also Hardener 5 is a cycloaliphatic amine which was said to have good chemical resistance but it has the worst performance. Its shelf life is 1 year, hardener would no longer be stable near expiration date so this result may be due to the usage time which may be through the expiring date.

Different rates of reactive diluents quantities (5 %, 10%, 15%) was used in sample mixtures. Performance increases with decreasing reactive diluent rate. This must be because of decreasing cross-linking density which would provide chemical resistance. Pure samples performed better than reactive diluent added ones.

In comparing the performances of the samples added reactive diluents with different functionalities, it was observed that trifunctional reactive diluents performed better than monofunctional and difunctional reactive diluents. And generally difunctional reactive diluents had the worst performance. As this type of reactive diluents gave the shortest pot-life results, also this result in chemical resistance may be because difunctional reactive diluent may increase the reactivity.

Some factors affecting chemical resistance are epoxy/curing agent ratio, curing temperature and choice of curing agent [37]. As it is previously mentioned high temperature curing provide better properties like better chemical resistance.

6.4 Pull-off Adhesion Test

For evaluating resin performances, it was seen that Bis A performs better than other resin types. It includes methyl groups rather than H as in Bis F and Bis A/F, this may be affected the performance.

Hardener performances was similar except hardener 2 which showed highly good performance, this may be because of its non-conjugated backbone. Hardener 3 performed also good. Benzyl alcohol addition increased the performance of hardener 5 which increases the effectiveness. Adhesion property of the resins are dependent on the hydroxyl pendants formed.

Reactive diluent addition decreased the performance as in other experiments because of their performance decreasing effect so generally as the reactive diluent addition rate decreases adhesion strength increased. But for reactive diluent added samples difunctional reactive diluent provided the highest adhesion strength whose results was similar with trifunctional reactive diluent, confirming the less performance decreasing effects of polyfunctional reactive diluents than monofunctional ones.

6.5 General Evaluation

In this study several test were applied both liquid resin mixtures and hardened state mixtures with different hardeners and different functionality reactive diluents for searching their effects. It was revealed that cross-linking density is the main property affecting performances. Resin type (Bisphenol A, Bisphenol F and Bisphenol A/F) didn't showed a great difference in experiment results. Reactive diluent addition rate and the functionality of reactive diluent has also effect on performances. High reactive diluent addition rates decreases the strength and surely decreases viscosity. Most strength decreasing effect was observed for monofunctional reactive diluent since it decreases the functionality of the system. Its effect was not observed for difunctional and trifunctional reactive diluents whose performances are similar, also sometimes they may increase the performance since they doesn't decrease the functionality.

Hardener is the most important component affecting the strength and durability. In this study aliphatic and cycloaliphatic type hardeners were used. Most important point for hardeners was their effectiveness for providing cross-linking. Best results were gained by hardener 3, and also hardener 1 and 2 showed good performance. Hardener 4 performed good when it is used with out activator addition. Oppositely hardener 5 performed better with activator addition. It shows that benzyl alcohol usage quantity is critical since it is an effective solvent for epoxy resin. It facilitates the mixing where the mixing is very important for effectiveness of hardener. Although hardeners are different from each other by providing different properties to the resin, performances were best evaluated by numerical results gained in bending and compression strength tests which are supporting the conclusion.

REFERENCES

[1] www.netcomposites.com

[2] **Brydson, J.A.,** 1995. Plastic Materials, Butterworth-Heinemann

[3] **Ercan, C.,** 1997. Epoksi Polimer Harç ve Betonlarının İşlenebilme Özellikleri , *Yüksek Lisans Tez*i, İTÜ Fen Bilimleri Enstitüsü, İstanbul

[4] www.vishay.com/brands/measurements_group/guide/glossary/epoxy.htm

[5] www.dow.com

[6] www.netcomposites.com/education.asp?sequence=12

[7] **Ellis, B.,** 1993. Chemistry and Technology of Epoxy Resins, Chapman & Hall, Newyork

[8] **Gannon, J.,** A. History and Development of Epoxy Resins, CIBA-GEIGY Corporation, Ardsley, N.Y.

[9] wey238ab.ch.iup.edu/olccii/student/Bisphenol%281%29.htm

[10] www.deltrex.com/products/p018.htm

[11] www.state.nj.us/health/eoh/rtkweb/2388.pdf#search='in%20 manufacture%20epoxy%20polycarbonate%20phenoxy%20 polysulfone%20certain %20polyester%20resins'

[12] www.epoxyproducts.com/chemistry.html

[13] **Saçak, M.,** 2002 .Polimer Kimyası, Gazi Kitapevi, Ankara

[14] **Lee, H. and Neville, K.,** 1967. Handbook of Epoxy Resins, McGraw-Hill Handbooks

[15] **Trout, J.,** 1997. Epoxy Injection In construction, The Aberdeen Group.

[16] www.epoxychemistry.com

[17] Vestamin TMD Data Sheet

[18] Degussa Vestamin V214 Data Sheet

[19] Huntsman Accelerator 960-1 Data Sheet

[20] Merck Data Sheet

[21] Huntsman Aradur22 Data Sheet

[22] Degussa Vestamin IPD Data Sheet

[23] en.wikipedia.org/

[24] www.tamms.com/ASTMC881_tip.html

[25] www.airproducts.com/nr/rdonlyres/d98dc0d1-5a4f-41b1-99ab 2cbe7aeb280b/0/waterborne_epoxy_systemsmvt. pdf#search='epoxy%20in%20civil%20engineering'

[26] www.pubs.asce.org/ceonline/ceonline02/0202feat.html

[27] www.pace-eng.com/Pace/Newsletter_Epoxy.htm

[28] **El-Hawary, M. and Al-Khaiat, H.,** 1998. Effect of Sea Water on Epoxy-Repaired Concrete, *Cement and Concrete Composites* **20**: 41-52

[29] **Saccani, A. and Magnaghi ,V. ,** 1999. Durability of epoxy resin-based materials for the repair of damaged cementitious composites, *Cement and Concrete Research*, **29** : 95-98

[30] Kukdo Hardeners Hand Book

[31] **Ribeiro, M. and Reis, J.,** 2003. Thermal Expansion of Epoxy and Polyester Polymer Mortars, Plain Mortars and Fibre-Reinforced Mortars, *Polymer Testing* ,**22** : 849-857

[32] **D 4060 -95**, Standard Test Method for Abrasion Resistance of Organic Coaings by the Taber Abraser,

[33] **EN 1542**, Bonding Strength by Pull-Off Adhesion Test for Rigid Materials According to

[34] **Dubois, R.B., Wang, D.S.,** 1993. Effect of Structure on Coating Performance Properties of Novel Alkylenedioxydiphenol Based Epoxy Resins. *Progress in Organic Coating*, **22** : 161-179

[35] **Allock, H.R.** ,2003 .Contemporary Polymer Chemistry, Prentice Hall.

[36] **Vecera, M. and Mleziva, J.** 1995. The influence of the molecular structure on the chemical resistivity of solventless and high-solid epoxy reins, *Progress in Organic Coatings*, **26**(2-4): 51-263

[37] **Wegmann, A.,** 1997. Chemical Resistance of Waterborne Epoxy/Amine Coatings, *Progress in Organic Coatings*, **32**(1) : 231-239

APPENDIXES

Table A.1: General test results for samples R1-R18 with hardener 3.

Sample	Resin Mixture	Epoxy Value	Visc. (cp)	Pot-Life(min)	Flow(mm)	1D. B/C Str.(MPa)	14D. B/C Str.(MPa)
R1	RFA30	0,5434	9500	31	138	24,59/83,73	26,38/97,00
R2	RA	0,5376	16700	39	142	18,53/75,94	26,71/97,21
R3	RF	0,584	5850	20	139	25,95/79,74	26,89/93,08
R4	RFA30 (% 90)+ RDMF(%10)	0,538	1150	75	170	19,64/46,38	23,69/78,18
R5	RFA30 (% 90)+ RDDF(%10)	0,578	2400	29	176	26,95/89,18	30,69/103,73
R6	RFA30 (%90)+RDTF (%10)	0,571	6200	55	157	25,96/71,75	29,33/90,87
R7	RA (% 90)+ RDMF(%10)	0,513	2000	57	177	22,9/59,99	23,33/62,74
R8	RA (% 90)+ RDDF(%10)	0,551	2600	40	272	25,29/80,03	28,05/97,77
R9	RA (%90)+RDTF (%10)	0,56	2440	42	150	30,48/87,92	28,04/98,34
R10	RF (% 90)+ RDMF(%10)	0,554	1100	51	171	22,65/49,15	20,99/58,76
R11	RF (% 90)+ RDDF(%10)	0,608	1200	33	205	28,05/97,77	29,14/95,24
R12	RF (%90)+RDTF (%10)	0,558	3500	15	144	27,64/71,64	27,82/76,42
R13	RFA30 (%95)+RDMF (%5)	0,553	4550	60	171	25,96/80,89	23,76/71,99
R14	RFA(%85)+ RDMF (%15)	0,524	900	75	201	19,42/44,37	21,69/58,27
R15	RA (%95)+RDMF (%5)	0,524	4700	53	174	24,11/81,87	23,3/74,05
R16	RA(%85)+RDMF (%15)	0,499	800	83	196	20,72/50	19,29/56,12
R17	RF(%95)+RDMF (%5)	0,567	1900	45	175	19,4/41,3	22,7/62,2
R18	RF(%85)+RDMF (%15)	0,542	540	64	204	27,67/77,88	19,48/48,79

Table A.2: Experiment results of mixtures containing hardener 6.

Sample	Resin Mix	Epoxy Value	Visc.(cp)	Pot-Life(min)	Flow(mm)	1D.B/C Str.(N/mm^2)	14D.B/CStr.(N/mm^2)
R1	RFA30	0,5434	9500	40	178	8,25/30,19	10,64/56,57
R2	RA	0,5376	16700	57	148	7,9/41,59	6,4/41,24
R3	RF	0,584	5850	34	191	8,32/40,46	10,83/58,55
R4	RFA30 (% 90)+ RDMF(%10)	0,538	1150	67	212	7,75/32,25	12,96/68,6
R5	RFA30 (% 90)+ RDDF(%10)	0,578	2400	63	192	8,43/39,6	13,32/67,57
R6	RFA30 (%90)+RDTF (%10)	0,571	6200	53	206	8,17/42	9,71/51,54
R7	RA (% 90)+ RDMF(%10)	0,513	2000	60	204	7,49/38,85	9.68/57,31
R8	RA (% 90)+ RDDF(%10)	0,551	2600	85	194	8,31/41,65	8,82/43,69
R9	RA (%90)+RDTF (%10)	0,56	2440	47	178	6,67/40,26	9,43/48,54
R10	RF (% 90)+ RDMF(%10)	0,554	1100	53	195	9,12/45,37	12,04/64,63
R11	RF (% 90)+ RDDF(%10)	0,608	1200	52	205	9,22/44,1	14,22/78,86
R12	RF (%90)+RDTF (%10)	0,558	3500	43	207	8,69/46,98	12,2/71,85
R13	RFA(%95)+RDMF (%5)	0,553	4550	61	197	7,93/37,41	10,68/52,53
R14	RFA(%85)+ RDMF (%15)	0,524	900	70	224	7,8/38,5	12,72/60,15
R15	RA (%95)+RDMF (%5)	0,524	4700	59	194	7,01/35,47	9,3/47,87
R16	RA(%85)+RDMF (%15)	0,499	800	120	233	6,49/37,48	12,24/63,87
R17	RF(%95)+RDMF (%5)	0,567	1900	50	195	8,37/41,1	14,91/73,18
R18	RF(%85)+RDMF (%15)	0,542	540	73	209	8,52/39,66	19,78/80,77

Table A.3: Experiment results of given samples.

Resin mix	Hardener mix	Quantity(g)	Flow(mm)	1D. B/C Str. (N/mm^2)	14D. B/C Str. (N/mm^2)	Pot life(min)
RA (100)	Har.2	34	195	12,49/75,17	16,07/82,01	74
RA+RDMF (10%)	Har.2	34	222	22,06/63,84	18,08/58,16	71
RA+RDDF (10%)	Har.2	34	225	24,71/73,4	28,93/80,38	93
RA+RDTF (10%)	Har.2	34	193	20,26/83,03	23,36/77,78	59
RA (100)	Har.1	40	194	10,05/40,10	17,77/43,46	40
RA+RDMF (10%)	Har.1	40	221	22,1/44,17	19,21/41,43	53
RA+RDDF (10%)	Har.1	40	221	23,97/61	24,97/56,93	86
RA+RDTF (10%)	Har.1	40	203	20,11/46,06	22,04/47,21	50
RA (100)	Har.5	42,6	205	4,5/26,39	5,62/32,25	114
RA+RDMF (10%)	Har.5	42,6	185	5,32/28,13	6,18/30,69	112
RA+RDDF (10%)	Har.5	42,6	215	4,93/22,21	4,92/27,43	175
RA+RDTF (10%)	Har.5	42,6	202	5,49/33,32	6,02/35,18	82
RA (100)	Har.5 (42.6)+10% Act.	52,6	204	7,81/44,2	9,58/45,62	48
RA+RDMF (10%)	Har.5 (42.6)+10% Act.	52,6	226	19,22/53,07	10,35/47,26	51
RA+RDDF (10%)	Har.5 (42.6)+10% Act.	52,6	224	9,23/37,26	18,96/48,36	63
RA+RDTF (10%)	Har.5 (42.6)+10% Act.	52,6	215	23,66/68,92	19,57/49,88	41
RA (100)	Har.4	37,2	185	22,25/39,63	24,17/53,68	169
RA+RDMF (10%)	Har.4	37,2	203	23,22/42,36	25,03/54,98	240++
RA+RDDF (10%)	Har.4	37,2	218	9,84/17,35	24,27/50,59	240++
RA+RDTF (10%)	Har.4	37,2	196	25,72/54,12	26,88/64,25	158
RA (100)	Har.4 (37,2)+30% Act.	67,2	224	6,12/10,43	5,36/7,54	50
RA+RDMF (10%)	Har.4 (37,2)+30% Act.	67,2	229	1,71/2,76	3,49/6,5	60
RA+RDDF (10%)	Har.4 (37,2)+30% Act.	67,2	242	1,51/2,42	4,13/7,82	57
RA+RDTF (10%)	Har.4 (37,2)+30% Act.	67,2	232	3,79/6,35	5,69/8,76	70

Note: The grey cells are results of two day strengths.

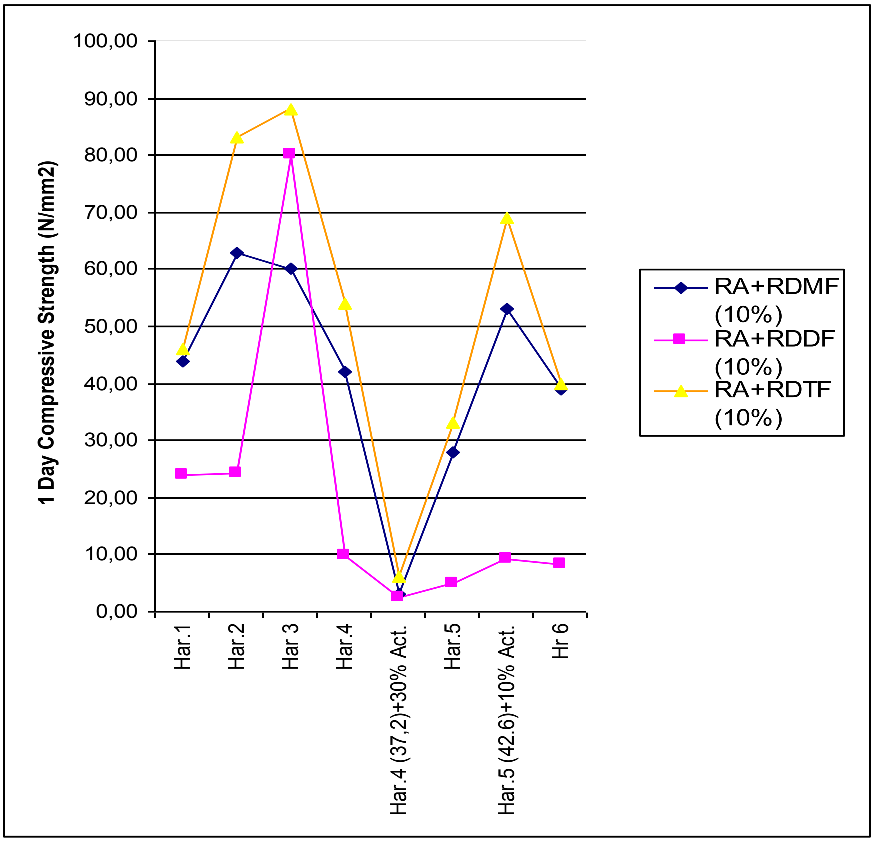


Figure B.1: 1 day compressive test results of samples with different hardeners and reactive diluents

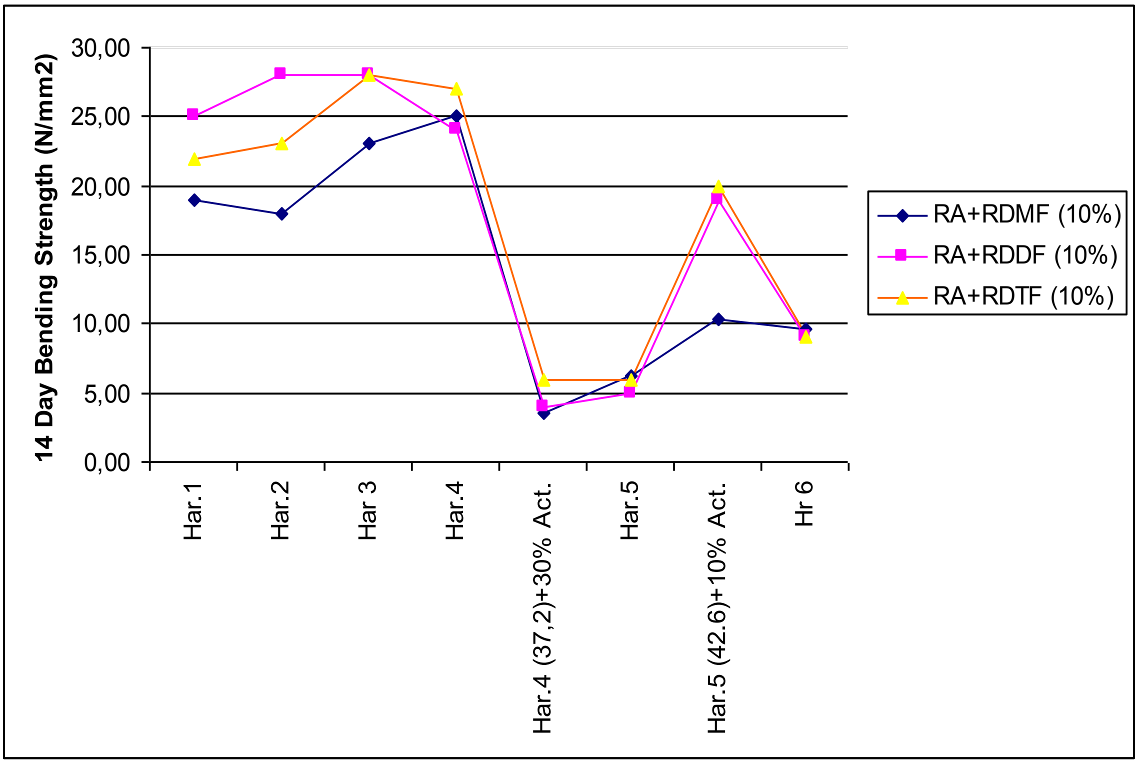


Figure B.2: 14 day bending test results of samples with different hardeners and reactive diluents

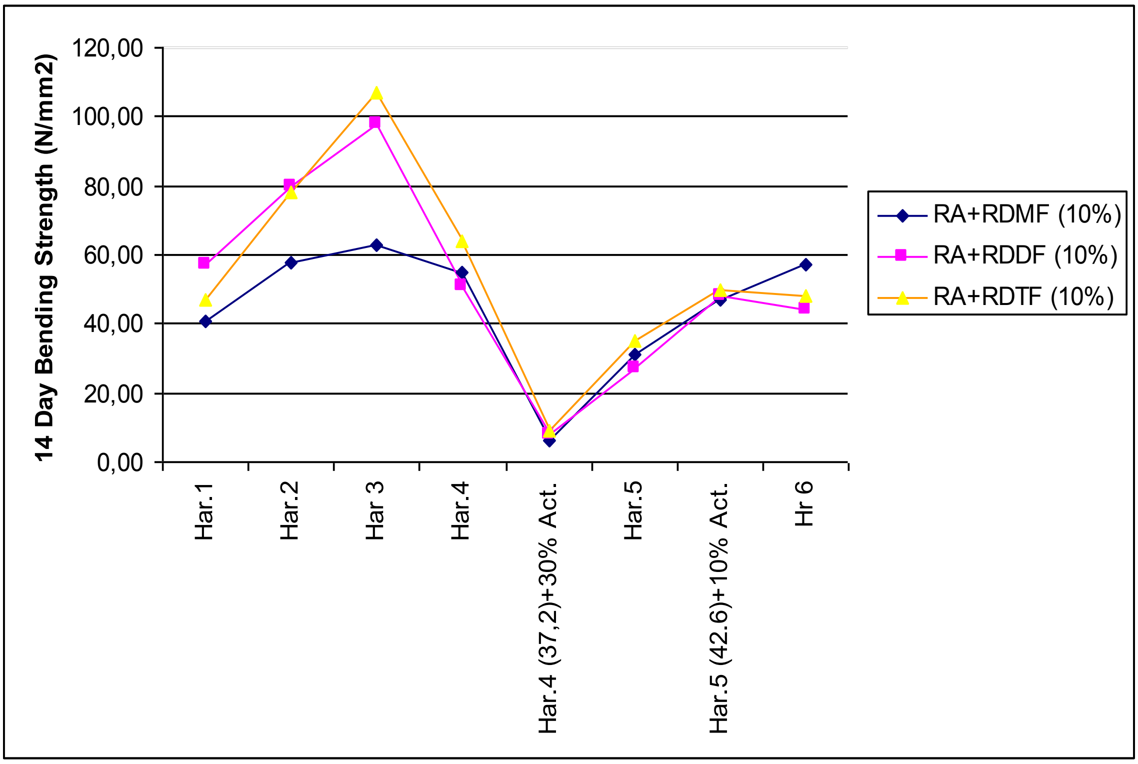


Figure B.3: 14 day compressive test results of samples with different hardeners and reactive diluents

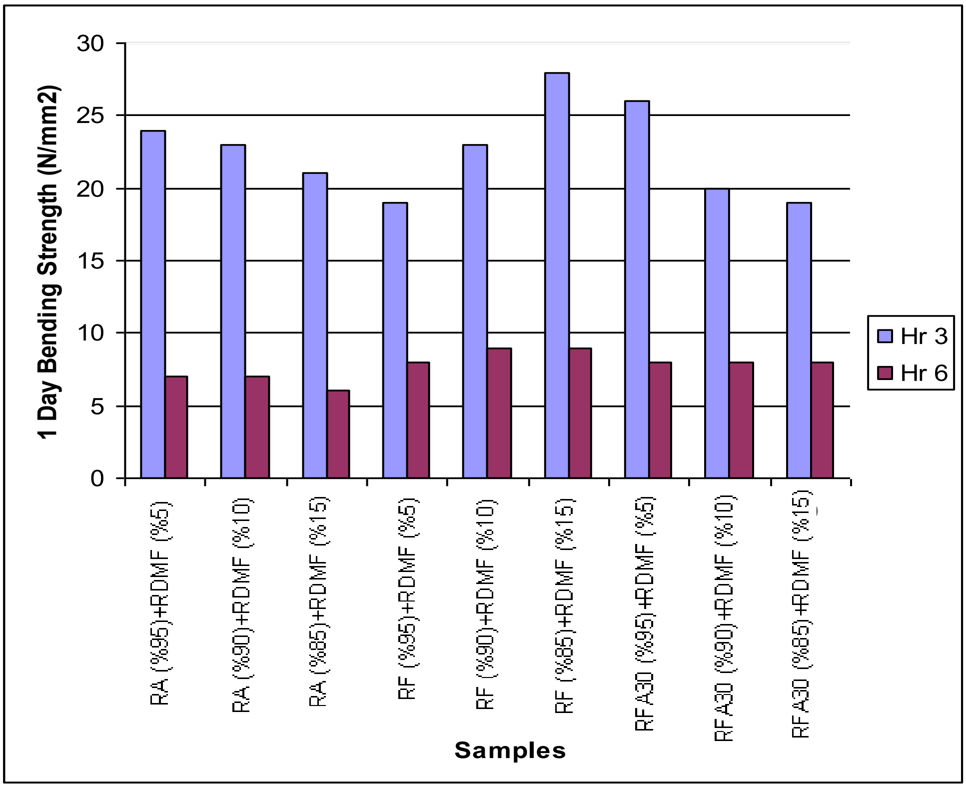


Figure B.4: 1 day bending test results of the given mixtures with hardener 3 and hardener 6.

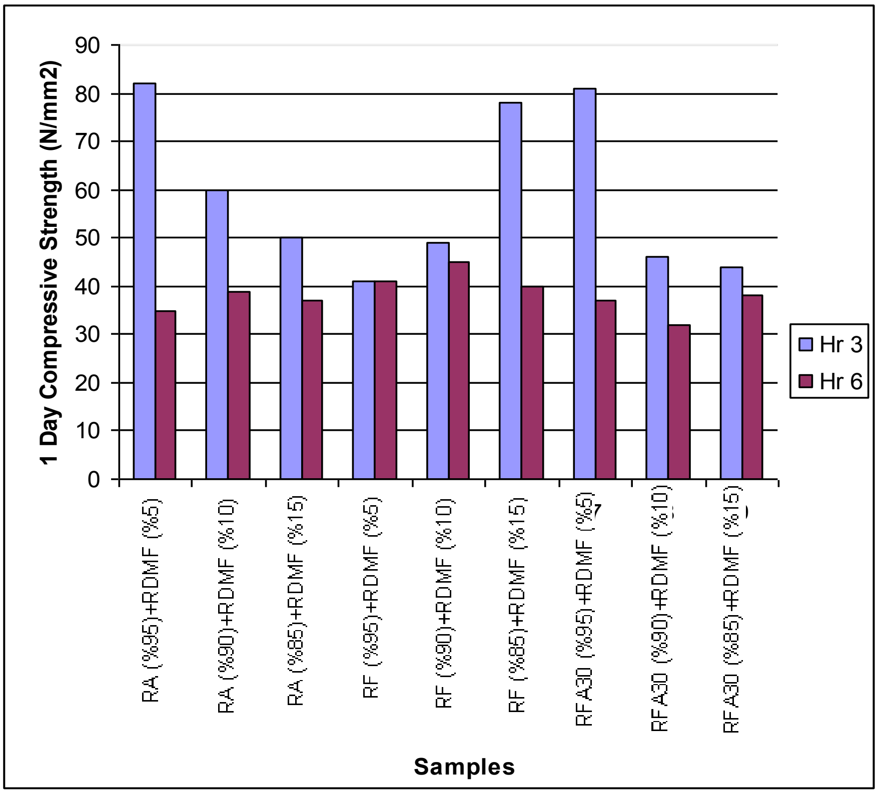


Figure B.5: 1 day compressive test results of the given mixtures with hardener 3 and hardener 6.

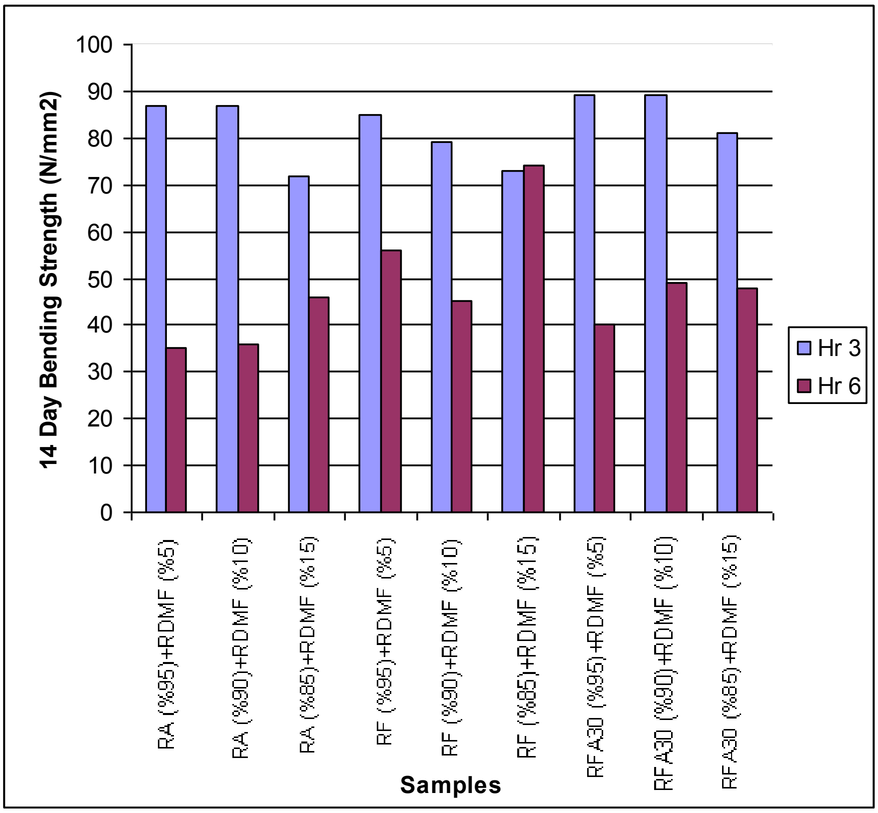


Figure B.6: 14 day bending test results of the given mixtures with hardener 3 and hardener 6.

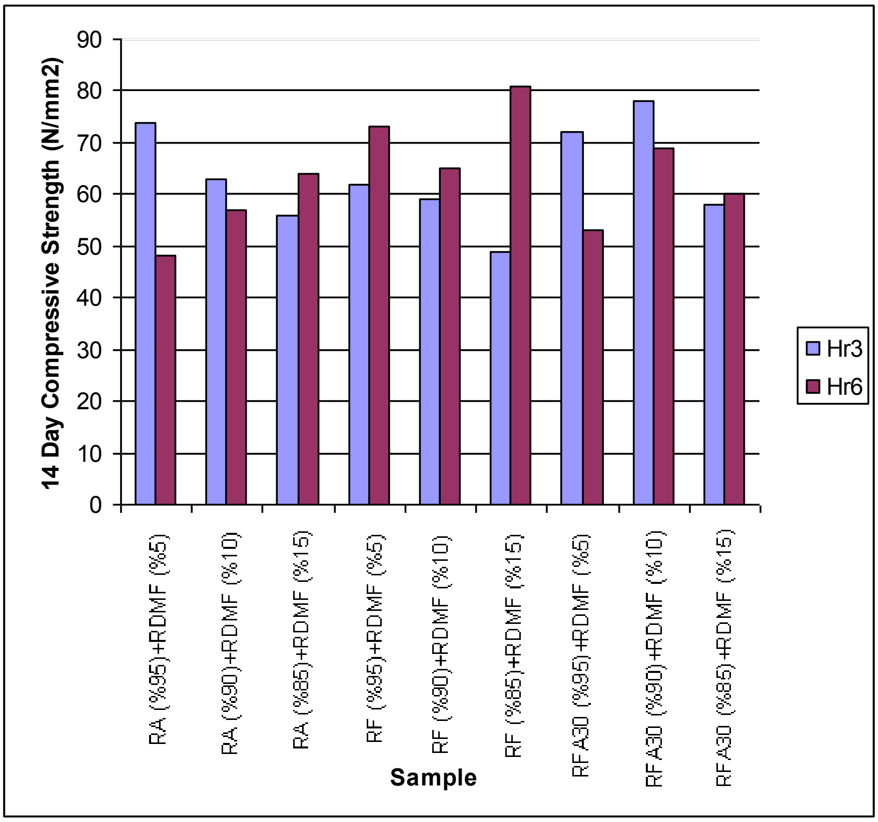


Figure B.7: 14 day compressive test results of the given mixtures with hardener 3 and hardener 6.

Table C.1: Photographs of the samples left in alcohol for 1 and 21 days.

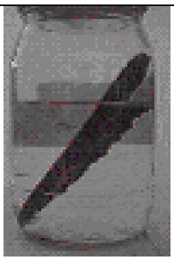
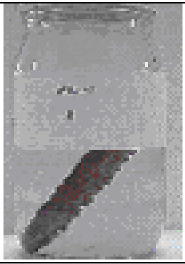
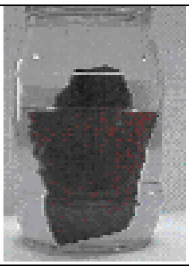
Sample No.	1	2	3	4	5
After 1 Day					
After 21 Days					
Sample No.	6	7	8	9	10
After 1 Day					
After 21 Days					
Sample No.	11	12	13	14	15
After 1 Day					
After 21 Days					

Table C.2: Photographs of the samples left in 37% formaldehyde solution for 1 and 21 days.

Sample No.	1	2	3	4	5
After 1 Day					
After 21 Days					
Sample No.	6	7	8	9	10
After 1 Day					
After 21 Days					
Sample No.	11	12	13	14	15
After 1 Day					
After 21 Days					

Table C.3: Photographs of the samples left in 15% lactic acid solution for 1 and 21 days.

Sample	1	2	3	4	5
After 1 Day					
After 21 Days					
Sample	6	7	8	9	10
After 1 Day					
After 21 Days					
Sample	11	12	13	14	15
After 1 Day					
After 21 Days					

Table C.4: Photographs of the samples left in 20% formic acid solution for 1 and 21 days.

Sample	1	2	3	4	5
After 1 Day					
After 21 Days					
Sample	6	7	8	9	10
After 1 Day					
After 21 Days					
Sample	11	12	13	14	15
After 1 Day					
After 21 Days					

Table D.1: One day compressive strengths of the HR3 samples

Code	Sample	Bending Compression	Bending (N/mm^2)	Comp. (N/mm^2)
R1	RFA 30 + HR3	B= 24,59	23,65	81,48
				89,25
			24,30	84,25
		C= 83,73		82,10
			25,84	81,66
				83,49
R2	RA + HR3	B= 18,53	18,11	79,76
				77,74
			19,30	69,73
		C= 75,94		77,29
			18,19	76,49
				74,67
R3	RF + HR3	B= 25,95	26,88	80,68
				80,59
			25,63	78,02
		C= 79,74		82,16
			25,33	79,30
				77,66
R4	RFA 30+ % 10 RDMF + HR3	B= 19,64	19,69	46,42
				49,54
			19,17	47,08
		C= 46,38		46,64
			20,07	44,25
				44,34
R5	RFA 30 + % 10 RDDF + HR3	B= 26,7	26,27	73,31
				72,42
			27,24	69,74
		C= 70,55		70,87
			26,60	67,27
				69,69
R6	RFA 30 + % 10 RDTF + HR3	B= 25,96	25,94	74,29
				72,56
			25,87	70,62
		C= 71,75		73,73
			26,06	68,34
				70,97
R7	RA + % 10 RDMF + HR3	B= 22,9	22,56	59,02
				62,61
			22,42	60,92
		C= 59,99		59,92
			23,71	60,73
				56,79
R8	RA + % 10 RDDF + HR3	B= 32,31	35,01	83,72
				93,67
			32,10	85,29
		C= 88,9		91,51
			29,91	90,92
				88,27
R9	RA + % 10 RDTF + HR3	B= 30,48	24,50	91,21
				74,67
			30,48	85,54
		C= 87,92		86,88
			34,08	87,80
				88,18

R10	RF + % 10 RDMF + HR3	B=22,65	22,85	50,16
				50,29
			23,05	49,28
		C= 49,15		44,98
			22,06	49,76
				50,43
R11	RF + % 10 RDDF + HR3	B=28,04	27,54	56,12
				62,39
			28,27	61,04
		C=59,98		60,46
			28,31	60,16
				59,70
R12	RF + % 10 RDTF + HR3	B=27,64	25,77	70,86
				71,12
			28,64	69,61
		C=71,64		72,67
			28,52	72,40
				73,16
R13	RFA30 + 5% RDMF+ Hr 3	B=25,96	24.65	80.97
				79.66
			27.11	81.76
		C=80,89		80.32
			26.12	82.02
				80.61
R14	RFA30 + 15 % RDMF+ Hr 3	B=19,42	18.69	43.71
				44.99
			19.71	45.05
		C=44,37		43.87
			19.86	43.09
				45.51
R15	RA + 5% RDMF + Hr 3	B=24,11	25.86	81.83
				83.01
			22.42	82.07
		C=81,87		79.37
			24.05	80.08
				84.86
R16	RA + 15 % RDMF + Hr 3	B=20,72	18,93	49,25
				51,62
			22,14	52,17
		C=50,00		48,12
			21,09	48,28
				50,56
R17	RF + 5% RDMF + Hr 3	B=19,44	19,9	43,03
				41,44
			19,15	39,86
		C=41,43		39,97
			19,27	40,89
				43,39
R18	RF + 15 % RDMF + Hr 3	B=27,67	27,38	76,12
				76,94
			27,54	76,8
		C=77,88		77,59
			28,09	79,78
				80,05

Table D.2: 14 day compressive strengths of the HR3 samples

Code	Sample	Bending Compression	Bending (N/mm^2)	Comp. (N/mm^2)
R1	RFA 30 + HR3	B= 26,38	26.03	100.39
				98.04
			24.49	99.03
		C= 97,00		97.18
			28.62	97.10
				90.28
R2	RA + HR3	B= 26,61	26.39	97.53
				103.97
			26.59	99.54
		C= 97,21		98.15
			26.85	91.12
				92.97
R3	RF + HR3	B= 26,89	26.18	94.45
				90.90
			27.20	92.46
		C= 93,08		92.14
			27.29	92.74
				95.80
R4	RFA 30+ % 10 RDMF + HR3	B= 23,69	24.58	77.87
				78.38
			24.32	83.67
		C= 78,18		82.79
			22.18	74.84
				71.50
R5	RFA 30 + % 10 RDDF + HR3	B= 27,33	26.22	87.36
				89.26
			27.82	93.60
		C= 89,95		93.89
			27.95	84.80
				90.80
R6	RFA 30 + % 10 RDTF + HR3	B= 29,33	29.30	89.46
				89.19
			28.81	91.72
		C= 90,87		93.31
			29.87	91.50
				90.02
R7	RA + % 10 RDMF + HR3	B= 23,33	24.53	73.42
				73.22
			21.77	64.10
		C= 62,74		62.95
			23.80	59.73
				64.18
R8	RA + % 10 RDDF + HR3	B= 28,99	29.00	97.26
				98.97
			28.22	95.18
		C= 98,69		105.62
			29.73	98.36
				96.74
R9	RA + % 10 RDTF + HR3	B= 28,04	28.50	101.17
				98.98
			27.85	103.10
		C= 98,34		96.05
			30.12	96.84
				93.93

R10	RF + % 10 RDMF + HR3	B=20,99	21.24	64.55
				56.07
			20.30	64.08
		C= 58,76		45.85
			21.42	60.92
				61.10
R11	RF + % 10 RDDF + HR3	B=28,24	28.87	80.98
				74.16
			27.04	75.83
		C=78,24		79.37
			26.48	82.73
				76.38
R12	RF + % 10 RDTF + HR3	B=27,82	28.03	76.42
				70.37
			27.76	80.79
		C=76,42		74.36
			27.68	81.79
				74.81
R13	RFA30 + 5% RDMF+ Hr 3	B=25,96	26.33	84.85
				77.57
			26.24	83.67
		C=80,89		80.82
			25.30	76.96
				81.49
R14	RFA30 + 15 % RDMF+ Hr 3	B=19,42	19.80	45.94
				45.02
			19.24	43.74
		C=44,37		44.78
			19.22	43.72
				42.99
R15	RA + 5% RDMF + Hr 3	B=24,11	25.55	82.60
				77.70
			21.71	80.93
		C=81,87		82.49
			25.08	84.21
				80.76
R16	RA + 15 % RDMF + Hr 3	B=20,72	20.54	42.37
				53.76
			20.93	51.30
		C=50		53.25
			20.69	49.81
				49.37
R17	RF + 5% RDMF + Hr 3	B=19,4	18.80	39.64
				42.22
			20.15	40.96
		C=41,3		42.70
			19.26	42.75
				39.54
R18	RF + 15 % RDMF + Hr 3	B=27,67	28.07	77.70
				82.81
			26.53	75.80
		C=77,88		76.07
			28,41	76.48
				76.54

Table D.3: 1 day compressive strengths of the HR6 samples

Code	Sample	Bending compression	Bending (N/mm^2)	Comp. (N/mm^2)
R1	RFA 30 + HR6	B=8,25	8,27	21,00
				37,89
			7,26	37,04
		C=30,19		38,18
			8,47	30,19
				34,22
R2	RA + HR6	B=7,9	7,22	37,90
				40,66
			8,14	44,41
		C=41,59		42,47
			8,34	39,20
				44,90
R3	RF + HR6	B=8,32	7,89	40,40
				41,99
			8,51	41,00
		C=40,46		38,37
			8,56	39,21
				41,79
R4	RFA 30+ % 10 RDMF + HR6	B=7,75	7,67	40,36
				34,04
			7,41	29,73
		C=32,25		39,92
			8,17	34,27
				37,44
R5	RFA 30 + % 10 RDDF + HR6	B=8,43	7,41	43,19
				40,31
			7,88	38,91
		C=39,6		31,67
			8,89	42,25
				32,43
R6	RFA 30 + % 10 RDTF + HR6	B=8,17	8,50	40,12
				44,35
			7,69	44,77
		C=42		41,42
			8,31	39,97
				36,34
R7	RA + % 10 RDMF + HR6	B=7,49	7,13	39,94
				37,57
			7,83	39,07
		C=38,85		36,88
			7,51	39,10
				40,54
R8	RA + % 10 RDDF + HR6	B=8,31	8,42	41,38
				31,43
			8,33	41,33
		C=41,65		44,24
			8,17	42,23
				34,36
R9	RA + % 10 RDTF + HR6	B=6,67	6,31	39,38
				43,80
			6,92	41,62
		C=40,26		38,11
			6,78	37,95
				40,70

R10	RF + % 10 RDMF + HR6	B=9,12	8,39	48,18
				44,10
			9,71	47,37
		C=45,37		43,55
			9,25	48,01
				41,04
R11	RF + % 10 RDDF + HR6	B=9,22	9,40	46,28
				41,65
			8,93	48,46
		C=44,1		41,40
			9,31	47,16
				35,43
R12	RF + % 10 RDTF + HR6	B=8,69	8,81	50,07
				49,85
			9,20	39,41
		C=46,98		45,54
			8,05	42,47
				51,24
R13	RFA30 + 5% RDMF+ HR6	B=7,93	7,79	33,34
				39,14
			8,5	37,75
		C=37,41		39,08
			7,5	38,94
				36,21
R14	RFA30 + 15 % RDMF+ HR 6	B=7,82	7,39	38,17
				41,97
			7,89	37,20
		C=38,5		40,20
			8,13	35,88
				37,57
R15	RA + 5% RDMF + HR 6	B=7,01	7,07	36,73
				32,54
			6,55	34,65
		C=35,47		37,27
			7,40	39,04
				33,19
R16	RA + 15 % RDMF + HR 6	B=6,94	7,48	32,21
				41,24
			6,90	33,20
		C=37,47		41,32
			6,44	37,30
				37,66
R17	RF + 5% RDMF + HR 6	B=8,37	9,23	41,58
				39,41
			7,84	39,03
		C=41,1		39,84
			8,04	43,15
				43,59
R18	RF + 15 % RDMF + HR 6	B=8,52	8,59	36,22
				38,05
			8,34	39,30
		C=39,66		40,63
			8,65	41,38
				42,36

Table D.4: 14 day compressive strengths of the HR6 samples

Code	Sample	Bending Compression	Bending (N/mm^2)	Comp. (N/mm^2)
R1	RFA 30 + Hr 6	B=10,64	9.98	54.33
				45.00
			10.67	59.63
		C=56,50		62.55
			11.27	49.99
				67.92
R2	RA + Hr 6	B=6,4	6.27	38.05
				40.97
			6.68	31.68
		C=41,24		42.07
			6.26	42.02
				43.08
R3	RF + Hr 6	B=10,83	9.95	62.76
				55.71
			10.81	55.16
		C=58,55		58.45
			9.87	50.07
				60.67
R4	RFA 30+ % 10 RDMF + Hr 6	B=12,96	11.07	64.09
				74.80
			14.36	69.91
		C=68,6		62.55
			13.45	64.99
				75.26
R5	RFA 30 + % 10 RDDF + Hr 6	B=13,32	14.22	66.98
				63.93
			10.6	71.22
		C=67,57		62.55
			15.14	64.99
				75.75
R6	RFA 30 + % 10 RDTF + Hr 6	B=9,71	9.11	56.98
				53.93
			7.94	51.22
		C=51,54		52.55
			12.08	45.99
				48.57
R7	RA + % 10 RDMF + Hr 6	B=9,68	9.98	59.28
				53.93
			7.78	51.22
		C=57,31		62.55
			11.28	47.49
				69.39
R8	RA + % 10 RDDF + Hr 6	B=8,82	8,90	45,60
				42,38
			8,78	42,99
		C=43,69		43,56
			8,77	43,04
				44,54
R9	RA + % 10 RDTF + Hr 6	B=9,43	9,62	49,80
				50,60
			9,33	49,79
		C=48,54		51,68
			9,35	44,09
				45,09

R10	RF + % 10 RDMF + Hr 6	B=12,04	12,39	69,90
				65,20
			12,40	70,94
		C=64,63		59,01
			11,39	61,59
				61,65
R11	RF + % 10 RDDF + Hr 6	B=14,22	12.67	72.03
				80.49
			14.88	81.22
		C=78,86		82.55
			15.11	87.49
				69.38
R12	RF + % 10 RDTF + Hr 6	B=12,2	11.82	74.27
				80.49
			11.67	71.02
		C=71,85		72.44
			13.11	67.30
				65.58
R13	RFA30 + 5% RDMF+ Hr 6	B=10,68	10,43	53,30
				51,99
			11,38	54,78
		C=52,53		51,90
			10,23	55,26
				47,96
R14	RFA30 + 15 % RDMF+ Hr 6	B=12,72	12,92	61,98
				57,88
			12,08	69,70
		C=60,15		61,10
			13,15	59,48
				60,22
R15	RA + 5% RDMF + Hr 6	B=9,3	9,30	39,44
				42,82
			9,29	47,71
		C=47,87		48,27
			8,77	50,12
				41,12
R16	RA + 15 % RDMF + Hr 6	B=12,24	12,54	73,90
				68,21
			12,22	62,59
		C=63,87		63,66
			11,74	62,21
				58,69
R17	RF + 5% RDMF + Hr 6	B=14,91	14,56	71,76
				86,61
			14,47	74,24
		C=73,18		69,96
			15,69	75,29
				74,66
R18	RF + 15 % RDMF + Hr 6	B=19,78	21,02	76,73
				88,60
			19,23	92,03
		C=80,77		71,88
			19,73	76,92
				80,94

Table D.5: 1 day compressive strengths of the samples including RDDF

Code	Sample	Bending Compression	Bending (N/mm^2)	Comp. (N/mm^2)
HR2	RA + 10% RDDF + Hr 2	B=24,71	23.97	75.18
				71.70
			25.70	73.73
		C=73,4		75.15
			24.47	72.42
				72.21
HR4	RA + 10% RDDF + Hr 1	B=23,97	23.69	62.89
				61.10
			18.47	56.52
		C=61		63.84
			24.95	63.49
				60.47
HR6	RA + 10% RDDF + Hr 3	B=25,29	24.68	73.32
				82.86
			26.87	80.91
		C=80,03		8.36
			24.31	79.69
				81.56
HR8	RA + 10% RDDF + Hr 6	B=8,31	8.20	41.38
				31.77
			8.33	41.33
		C=41,65		44.24
			8.17	42.23
				34.36
HR10	RA + 10% RDDF + Hr 5	B=4,93	5.26	23.15
				18.01
			4.90	21.37
		C=22,21		21.43
			4.63	22.88
				24.51
HR12	RA + 10% RDDF+Hr 5+10% Act	B=9,23	9.43	36.04
				37.56
			11.00	38.33
		C=37,26		39.49
			9.00	32.26
				34.87
HR14	RA + 10% RDDF+ Hr 4	B=9,84	10.00	17.55
				17.28
			8.34	14.90
		C=17,35		16.78
			9.67	17.21
				17.84
HR16	RA + 10% RDDF+ Hr 4+30%Act	B=1,51	1.48	2.42
				2.45
			1.43	2.28
		C=2,42		2.45
			1.54	2.39
				2.44

Table D.6: 14 compressive strengths of the samples including RDDF

Code	Sample	Bending Compression	Bending (N/mm^2)	Comp. (N/mm^2)
HR2	RA + 10% RDDF + Hr 2	B=28,93	27.85	82.81
				81.91
			30.19	77.74
		C=80,38		79.45
			28.75	77.47
				82.92
HR4	RA + 10% RDDF + Hr 1	B=24,97	27.02	55.79
				58.12
			23.98	56.63
		C=56,93		54.02
			23.91	57.50
				56.25
HR6	RA + 10% RDDF + Hr 3	B=28,05	29.80	96.86
				99.29
			28.47	85.34
		C=97,77		96.72
			25.89	98.74
				97.16
HR8	RA + 10% RDDF + Hr 6	B=8,82	8.90	45.60
				42.38
			8.78	42.99
		C=43.69		43.56
			8.77	43.04
				44.54
HR10	RA + 10% RDDF + Hr 5	B=4,92	4.90	27.42
				31.19
			5.25	27.77
		C=27,43		28.06
			11.64	26.48
				23.43
HR12	RA + 10% RDDF+Hr 5+10% Act	B=18,96	18.12	45.57
				45.75
			18.74	49.80
		C=48,36		50.29
			20.02	50.50
				48.24
HR14	RA + 10% RDDF+ Hr 4	B=24,27	21.89	49.44
				49.16
			25.27	52.48
		C=50,59		51.38
			25.65	49.99
				51.40
HR16	RA + 10% RDDF+ Hr 4+30%Act	B=4,13	4.40	7.59
				7.54
			3.90	6.72
		C=7,82		6.66
			4.10	6.77
				6.82

Cirriculum Vitae

Eren Özeren was born at 1982 in Istanbul. She started her education at 1988 with Çavuşoğlu Collage and graduated at 1992. She graduated from Beşiktaş Atatürk Anatolian High School at 1999. She completed her license education at Yıldız Technical University at “Metallurgy and Materials Engineering” program, graduated from “materials option”. After her graduation she started “Polymer Science and Technology Master Program” at Istanbul Technical University.