paintistanbul TURKCOAT CONGRESS

Synthesis and Characterization of Biobased Hyperbranched Polyesteramide Resin with Improved Scratch Resistance

Fevzi GÜL
Supervisor: Prof. Serkan EMİK / Prof. Mehmet Ali GÜRKAYNAK

İstanbul University – Cerrahpaşa
Institute of Graduate Studies
Department of Chemical Engineering – Chemical Technologies
Master Thesis

December, 2023

CONTENT

1. Literature Review
2. Aim of the Study
3. Experimental
4. Results and Discussion
5. Conclusions

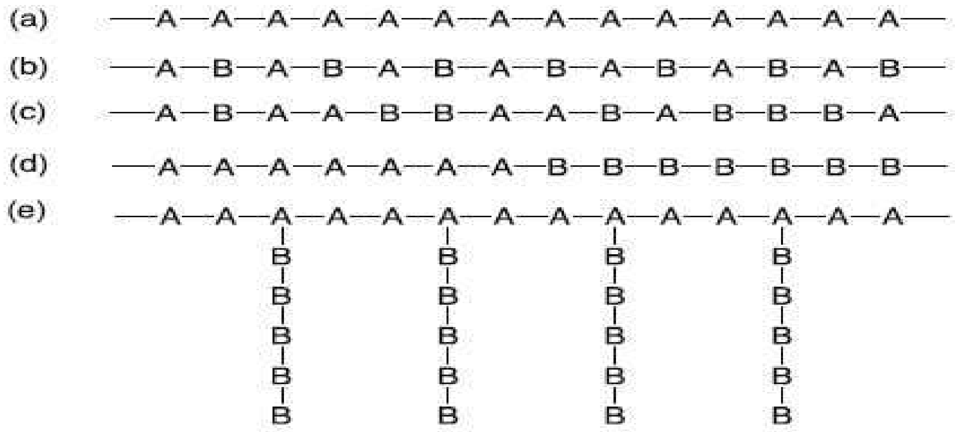
1. LITERATURE REVIEW

Polymers can be classified in various ways.

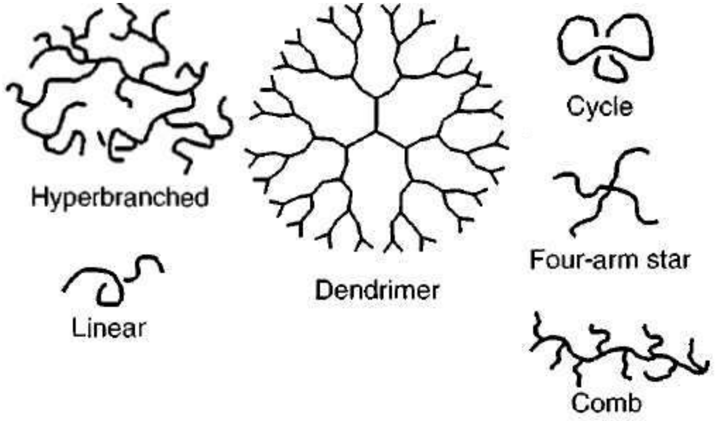
Polymers with different architectures can be synthesized besides linear polymers.

If the concentration of junction points is high enough, polymer molecule becomes a three-dimensional network.

Hyperbranched polymers can be formed by suppressing the cross-linking of branches.



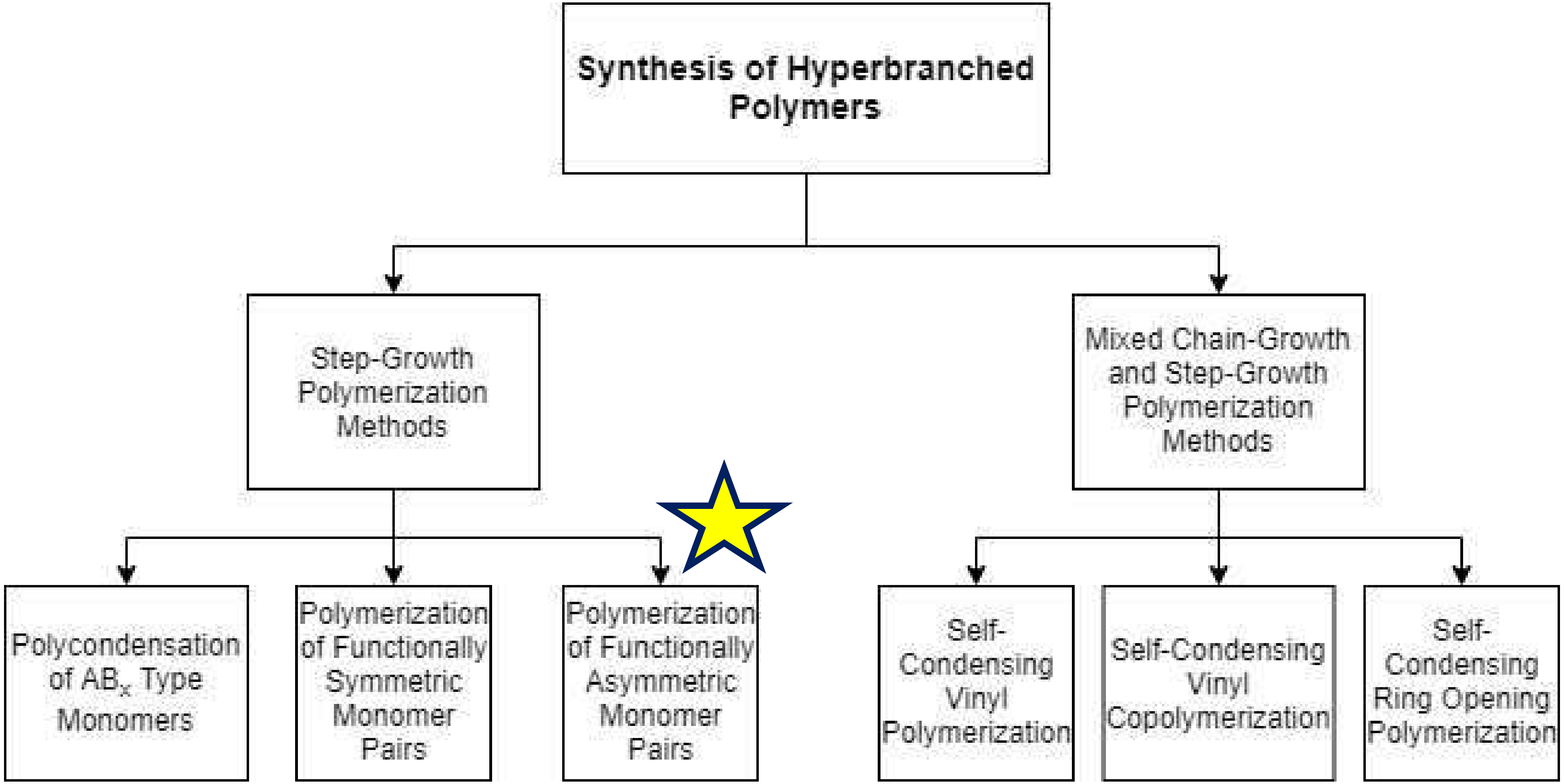
(a) homopolymer, (b) alternating copolymer, (c) random copolymer, (d) block copolymer, (e) graft copolymer



1. LITERATURE REVIEW

Dendrimers	Hyperbranched Polymers
Uniformly branched, three-dimensional tree-like structured globular-shaped macromolecules	Globular highly branched macromolecules but exhibit irregularity in structure and branching.
Degree of branching = 1	Degree of branching < 1
Multistep synthesis process	One-pot synthesis technique
Tedious and costly production	Less complicated and quite cost-effective production
Very low yield, not feasible for large scale production	Quite high yield, feasible for large scale production

1. LITERATURE REVIEW



1. LITERATURE REVIEW

Degree of Branching

It is a very important parameter to quantitatively characterize the hyperbranched polymers.

For this purpose, NMR analysis can be done to determine it directly.

Solution Properties

Both melt and solution viscosity of hyperbranched polymers are quite low because of the lack of chain entanglement.

Molecular Weight and Polydispersity

Hyperbranched polymers have higher molecular weight and polydispersity compared to their linear analogues.

MALS detector should be used in order to determine the molecular weight and polydispersity of hyperbranched polymers.

Thermal Properties

Increment in degree of branching reduces crystalline region in polymers.

There are also other parameters that affect the glass transition temperature of polymers like polarity of terminal group, rigidity of polymer backbone and steric hindrance.

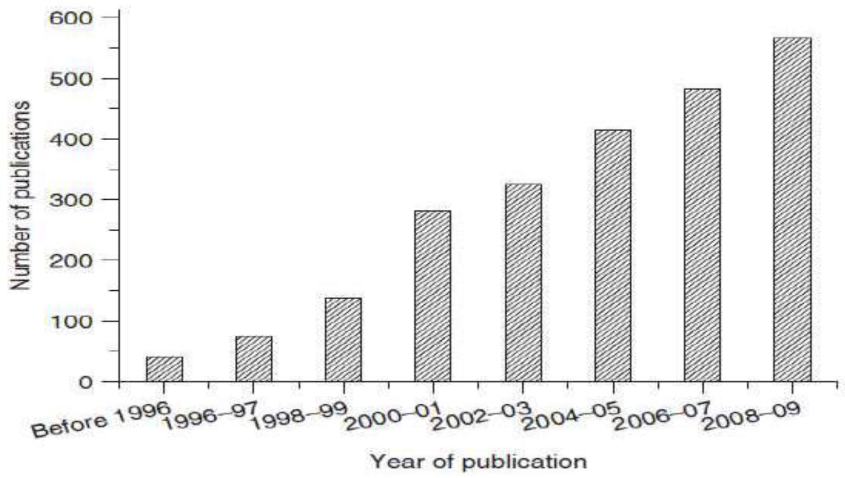
Rheological Properties

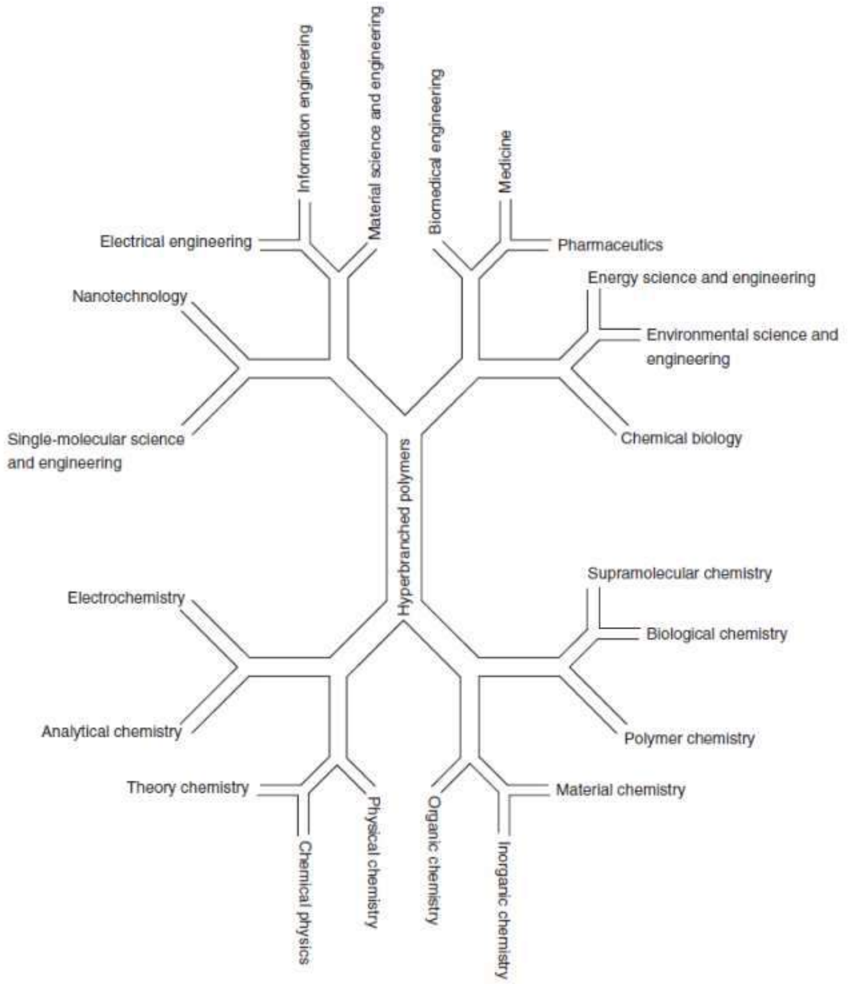
Due to lack of entanglements, hyperbranched polymers behave as Newtonian fluids.

1. LITERATURE REVIEW

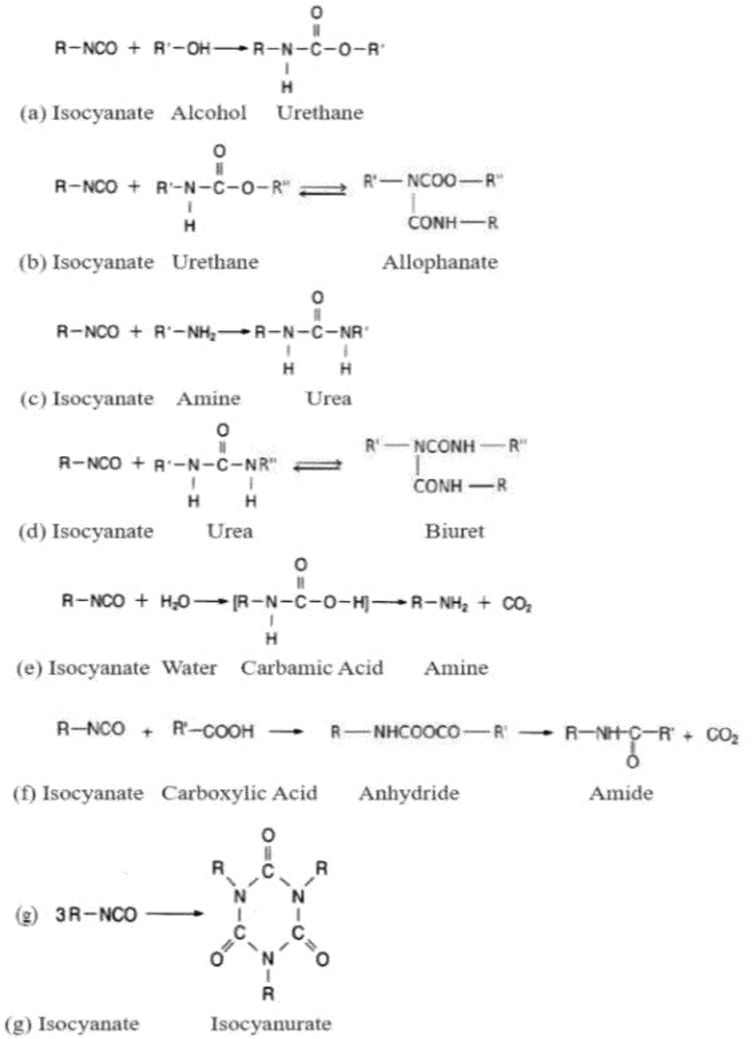
Applications

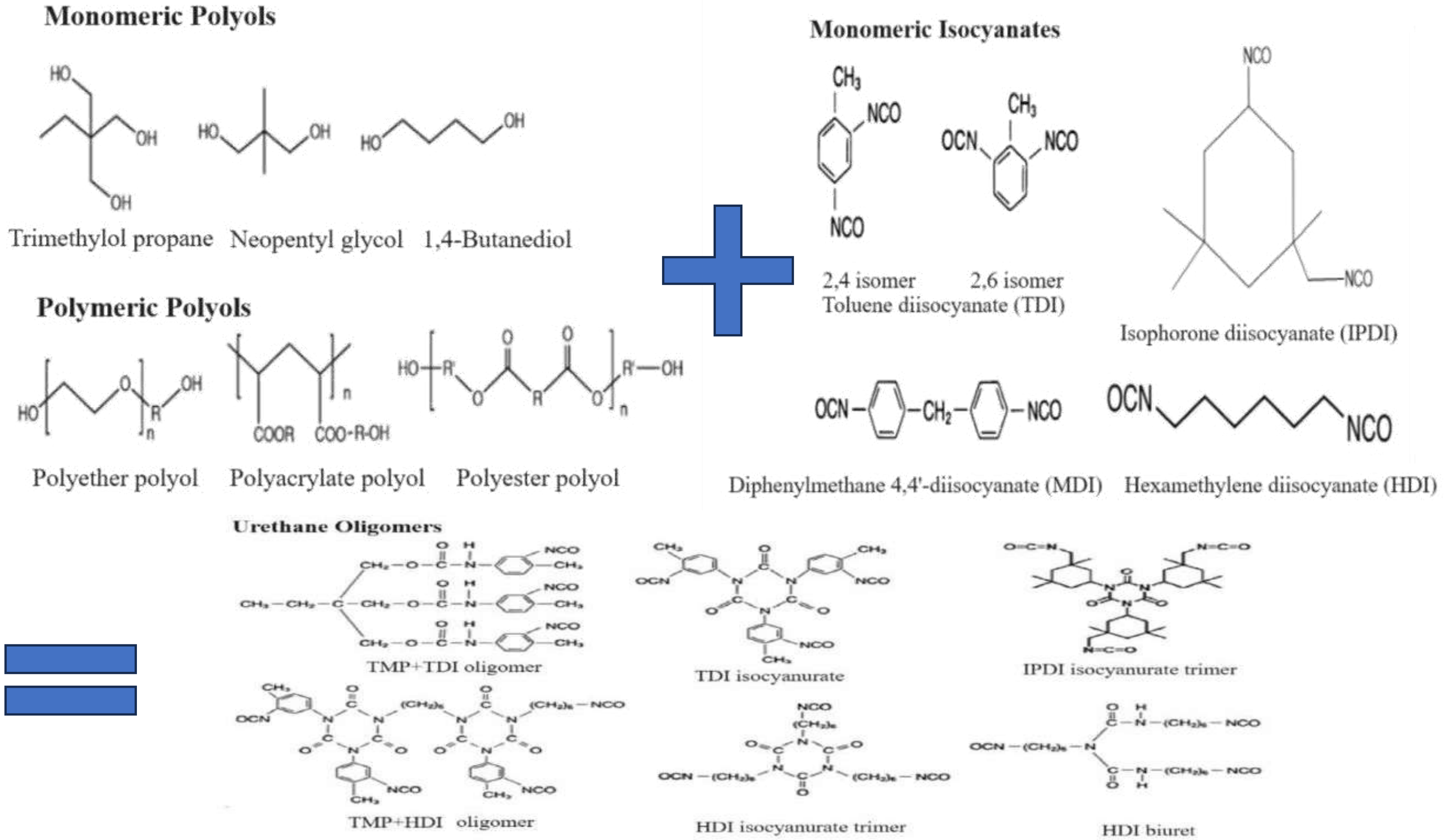
1. Coating and Resin
2. Additives
3. Nanocomposite and Nanohybrid
4. Thin Films and Sensorics





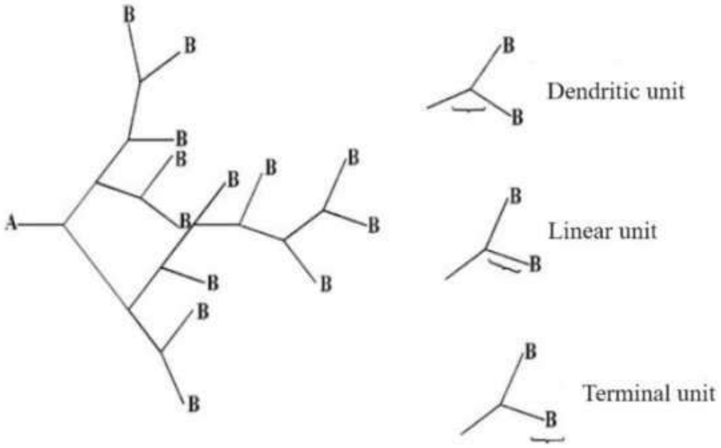
1. LITERATURE REVIEW



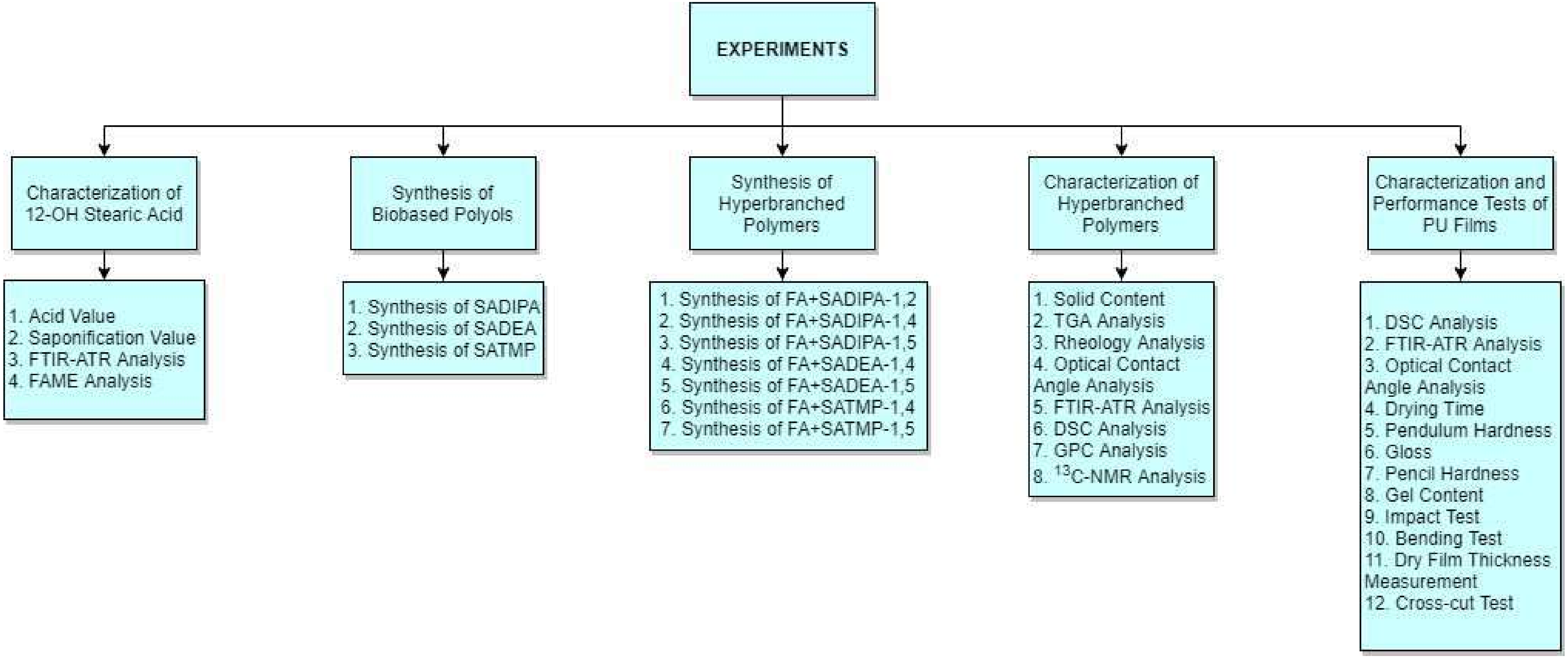


2. AIM of the STUDY

1. Decreasing the consumption of petrochemical feedstock
2. Synthesizing biobased polyols
3. Synthesizing hyperbranched polymers
4. Increasing the scratch resistance of 2K PU coatings



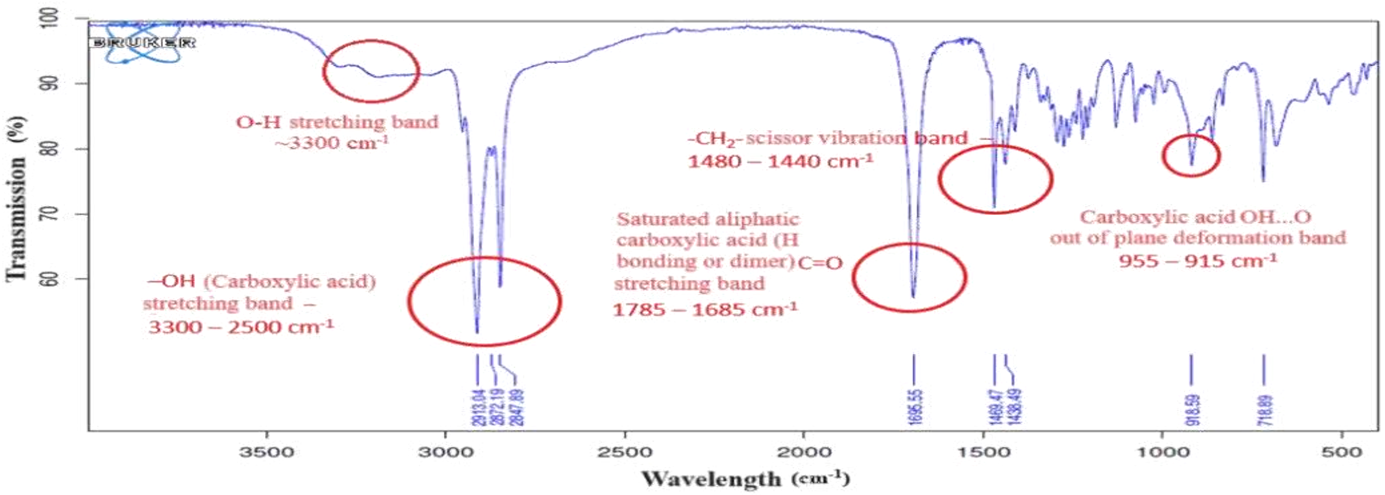
3. EXPERIMENTAL

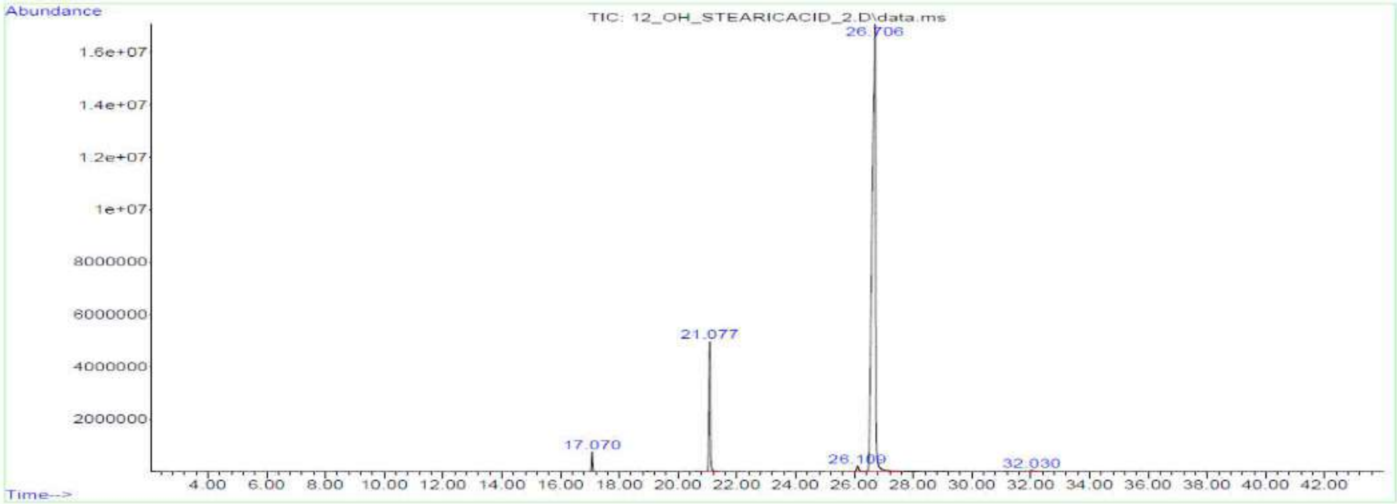


4. RESULTS and DISCUSSION

Characterization of 12-OH Stearic Acid

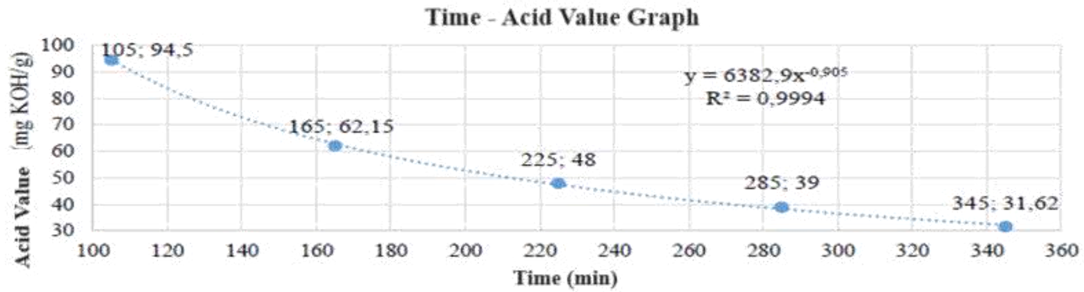
Analysis	Results
Acid Value	184,57 mg KOH/g
Saponification Value	188,36 mg KOH/g
Fatty Acid Composition	C16:0 - %1,08 C18:0 - %10,49 C18(12-OH):0-%88,24 C20:1 - %0,19
Molecular Weight	298,36 g/mol
Hydroxyl Content	%5,03
Hydroxyl Number	166 mg KOH/g

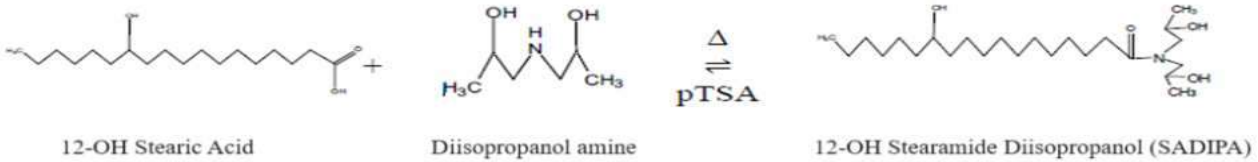




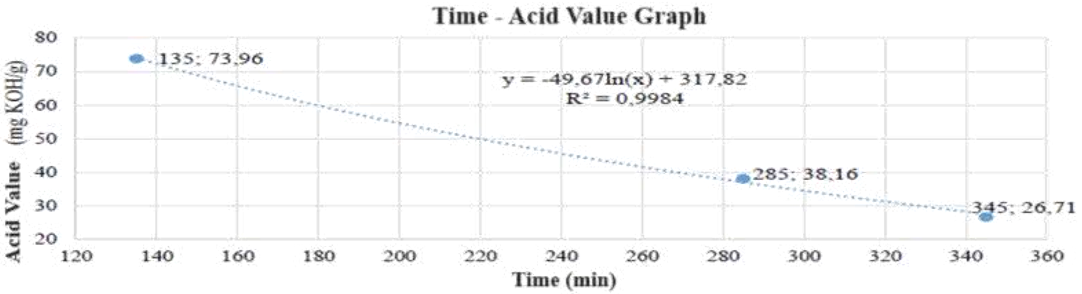
4. RESULTS and DISCUSSION

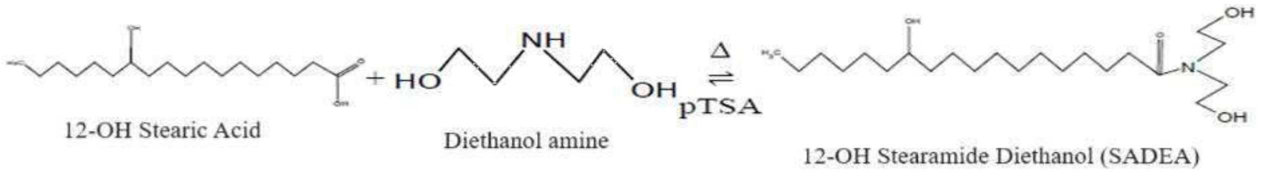
Synthesis of Biobased Polyols



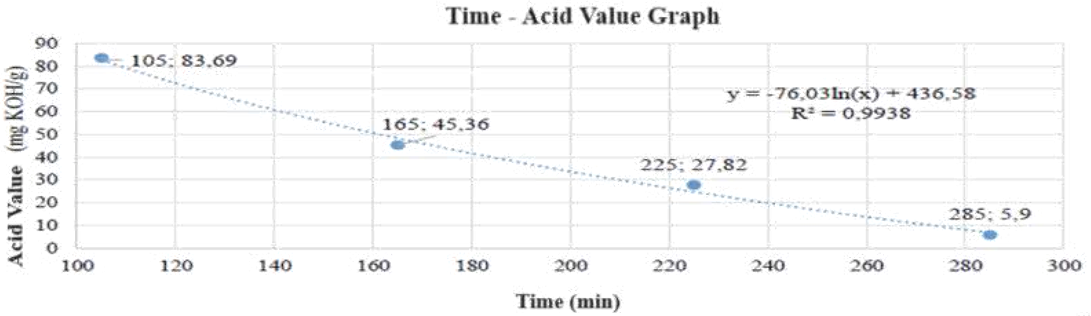


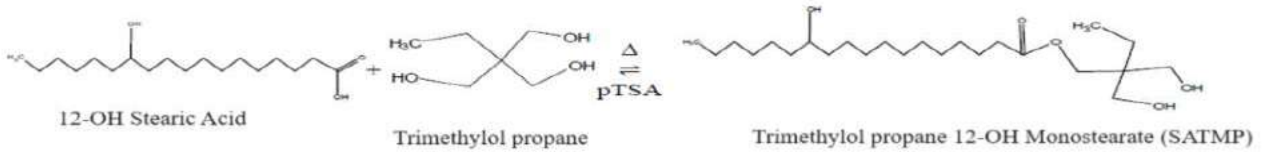
$$m_{\text{Fatty acid}} + m_{\text{Diisopropanol amine}} - m_{\text{Water}} = m_{SADIPA}$$
$$298{,}36 + 133{,}19 - 18 = 413{,}55 \text{ g/mol}$$





$$m_{\text{Fatty acid}} + m_{\text{Diethanol amine}} - m_{\text{Water}} = m_{SADEA}$$
$$298{,}36 + 105{,}14 - 18 = 385{,}5 \text{ g/mol}$$





$$m_{\text{Fatty acid}} + m_{\text{Trimethylol propane}} - m_{\text{Water}} = m_{SATMP}$$
$$298{,}36 + 134{,}17 - 18 = 414{,}53 \text{ g/mol}$$

4. RESULTS and DISCUSSION

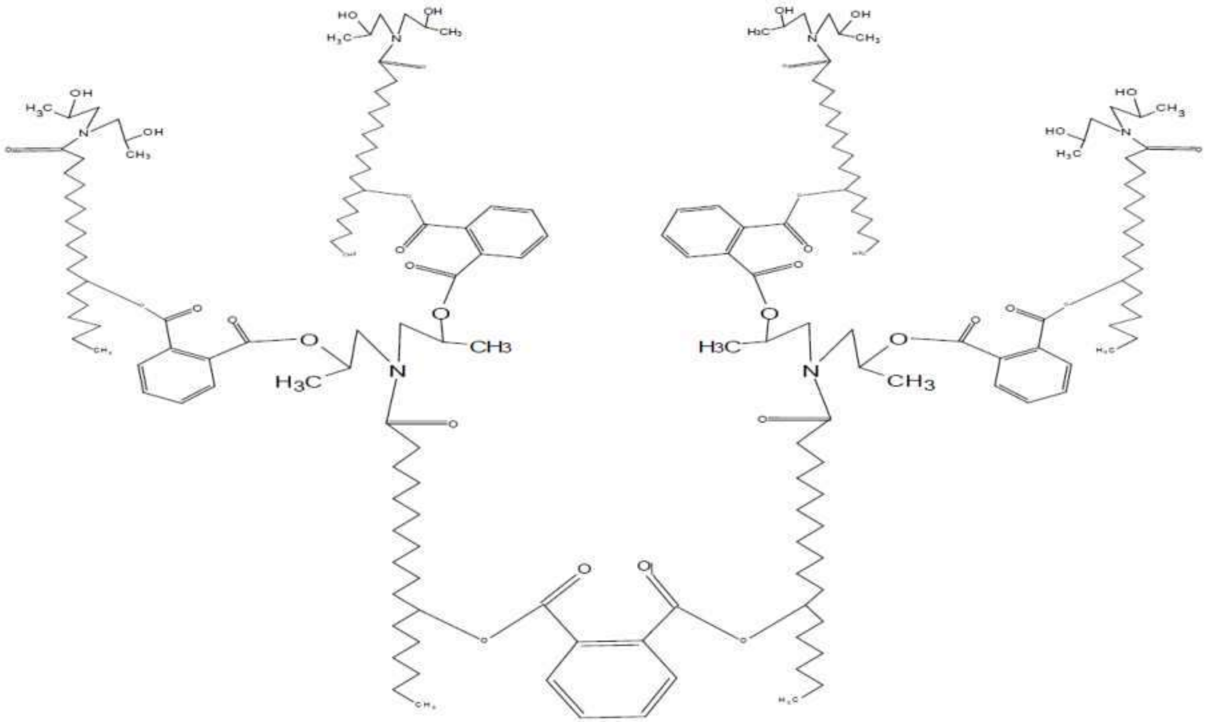
Synthesis of Hyperbranched Polymers

Phthalic anhydride was reacted with %20, %40 and %50 mole of excess SADIPA polyol, respectively.

Excess Polyol by Mole / Spect.	%20	%40	%50
Acid Value (mg KOH/g)	16	20,07	22,5
Hydroxyl Content (%)	4,34	5,21	5,61
Hydroxyl Equivalent Weight (g)	391,70	326,40	303,1

$$\underset{SADİPA}{6\,C_{24}H_{49}NO_4} + \underset{\text{Phthalic Anhydride}}{5\,C_8H_4O_3} \rightleftharpoons \underset{FA+SADIPA-1,2}{1\,C_{184}H_{304}N_6O_{34}} + \underset{\text{Water}}{5\,H_2O}$$

Theoretical molecular weight = 3131,8 g/mol



Molecular formula of FA+SADIPA-1,2

4. RESULTS and DISCUSSION

Synthesis of Hyperbranched Polymers

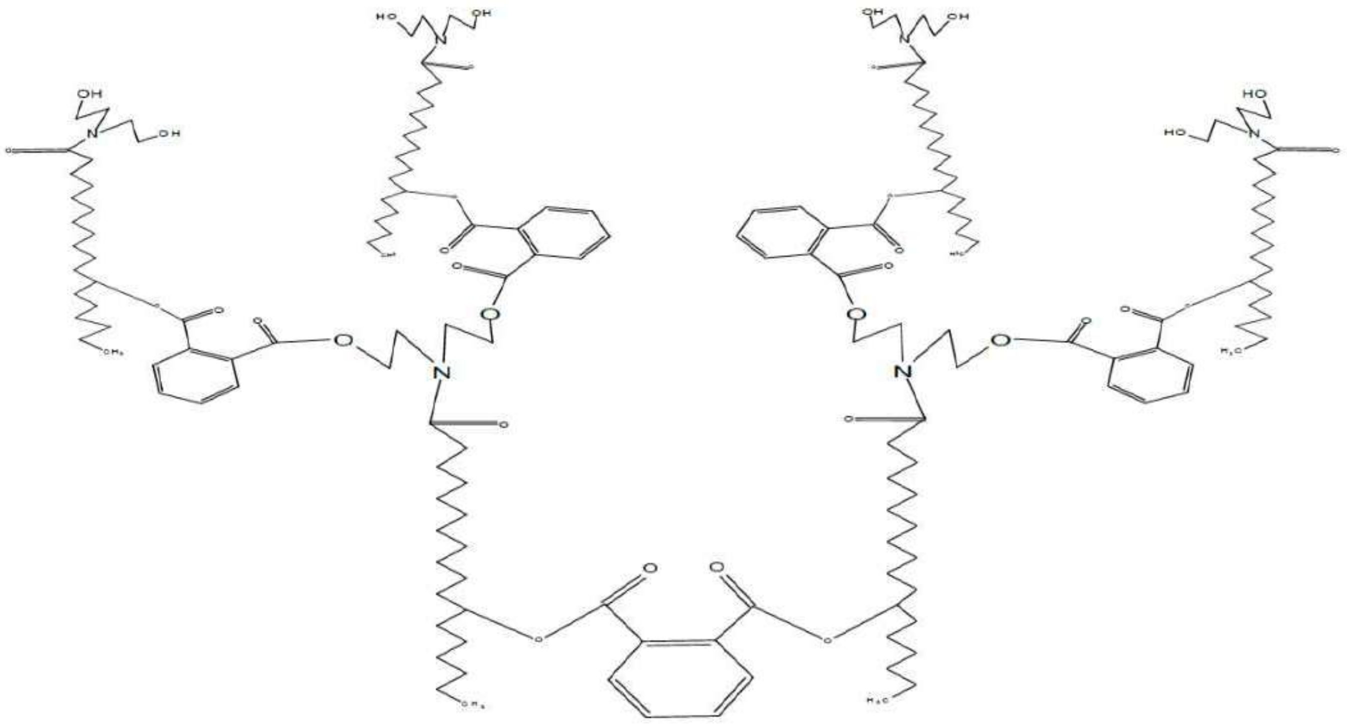
Phthalic anhydride was reacted with %20, %40 and %50 mole of excess SADEA polyol, respectively.

Excess Polyol by Mole / Spect.	%20	%40	%50
Acid Value (mg KOH/g)	GEL	28,3	22,06
Hydroxyl Content (%)		5,51	5,93
Hydroxyl Equivalent Weight (g)		308,63	286,6

$$6\ C_{22}H_{45}NO_4 + 5\ C_8H_4O_3 \rightleftharpoons 1\ C_{172}H_{280}N_6O_{34} + 5\ H_2O$$

SADEA   Phthalic Anhydride   FA+SADEA−1,2   Water

Theoretical molecular weight = 2963,5 g/mol



Molecular formula of FA+SADEA-1,2

4. RESULTS and DISCUSSION

Synthesis of Hyperbranched Polymers

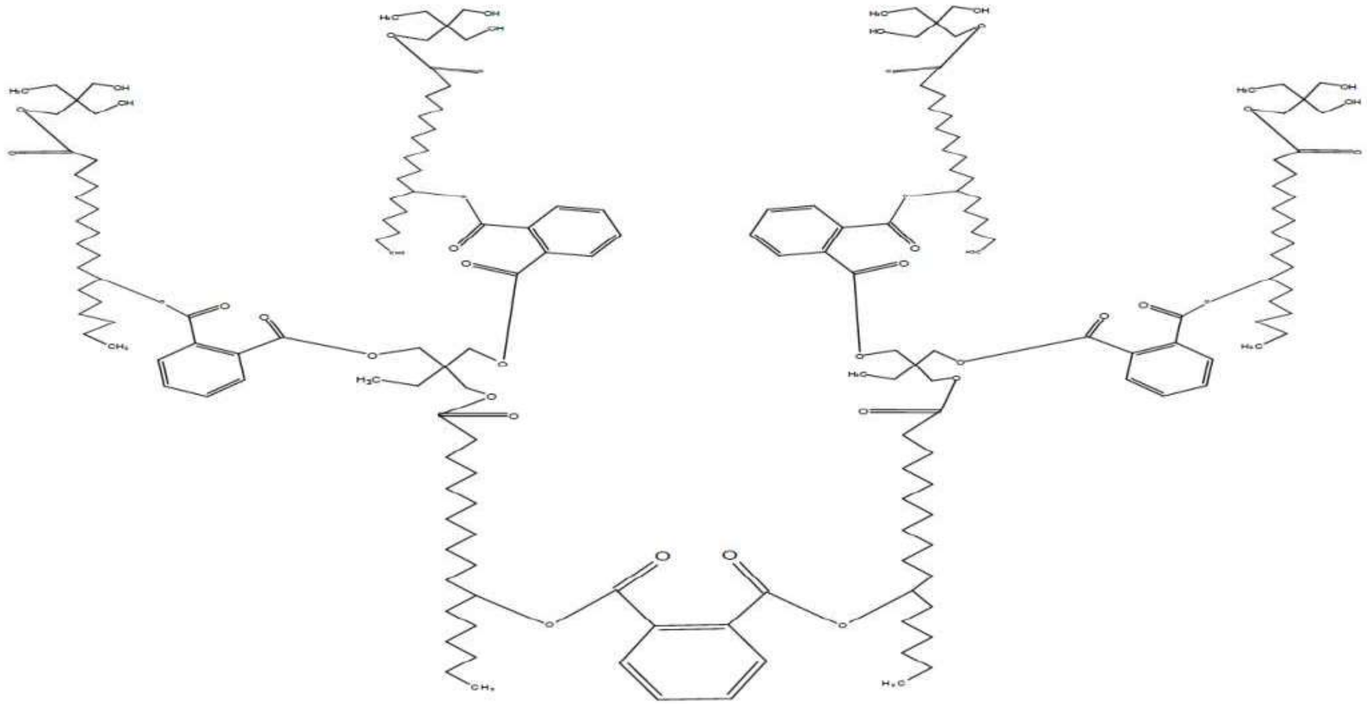
$$6\ C_{24}H_{48}O_5 \quad + \quad 5\ C_8H_4O_3 \quad \rightleftharpoons \quad 1\ C_{184}H_{298}O_{40} \quad + \quad 5\ H_2O$$

SATMP Phthalic Anhydride *FA+SATMP*−1,2 Water

Theoretical molecular weight = 3137,68 g/mol

Phthalic anhydride was reacted with %40 and %50 mole of excess SATMP polyol, respectively.

Spect. \ Excess Polyol by Mole	%40	%50
Acid Value (mg KOH/g)	22,78	22,89
Hydroxyl Content (%)	5,20	5,60
Hydroxyl Equivalent Weight (g)	327,16	303,80



Molecular formula of FA+SATMP-1,2

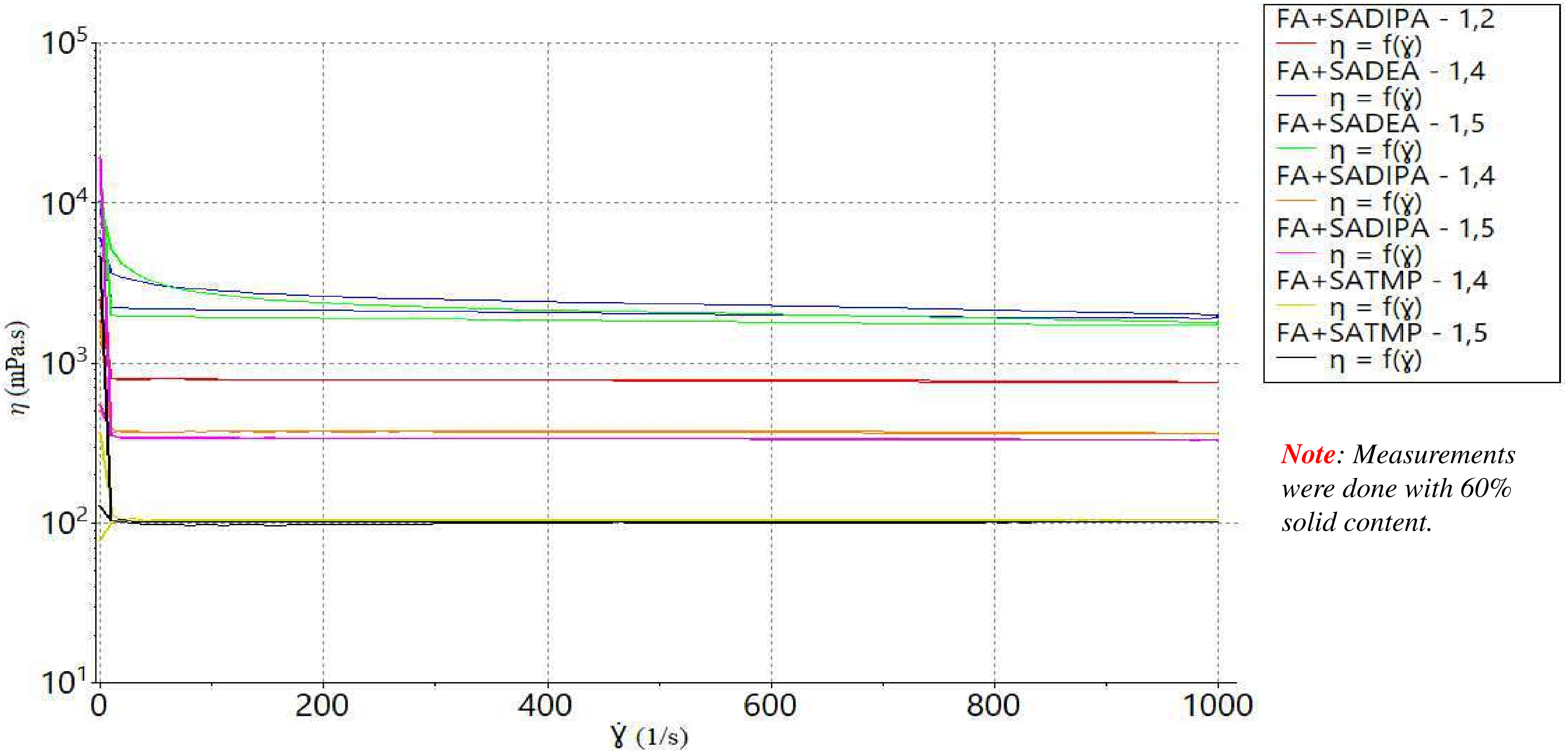
4. RESULTS and DISCUSSION

Characterization of Hyperbranched Polymers

Hyperbranched Polymers	Solid Content (%)	Thermal Decomposition Temperature (°C)	Thermo-oxidative Decomposition Temperature (°C)
FA+SADIPA-1,2	77,84	266,02	262,73
FA+SADIPA-1,4	77,85	268,79	254,28
FA+SADIPA-1,5	73,83	269,28	252,75
FA+SADEA-1,4	77,80	285,19	276,93
FA+SADEA-1,5	82,03	280,63	272,02
FA+SATMP-1,4	73,86	257,19	239,35
FA+SATMP-1,5	72,39	254,41	240,60

4. RESULTS and DISCUSSION

Characterization of Hyperbranched Polymers

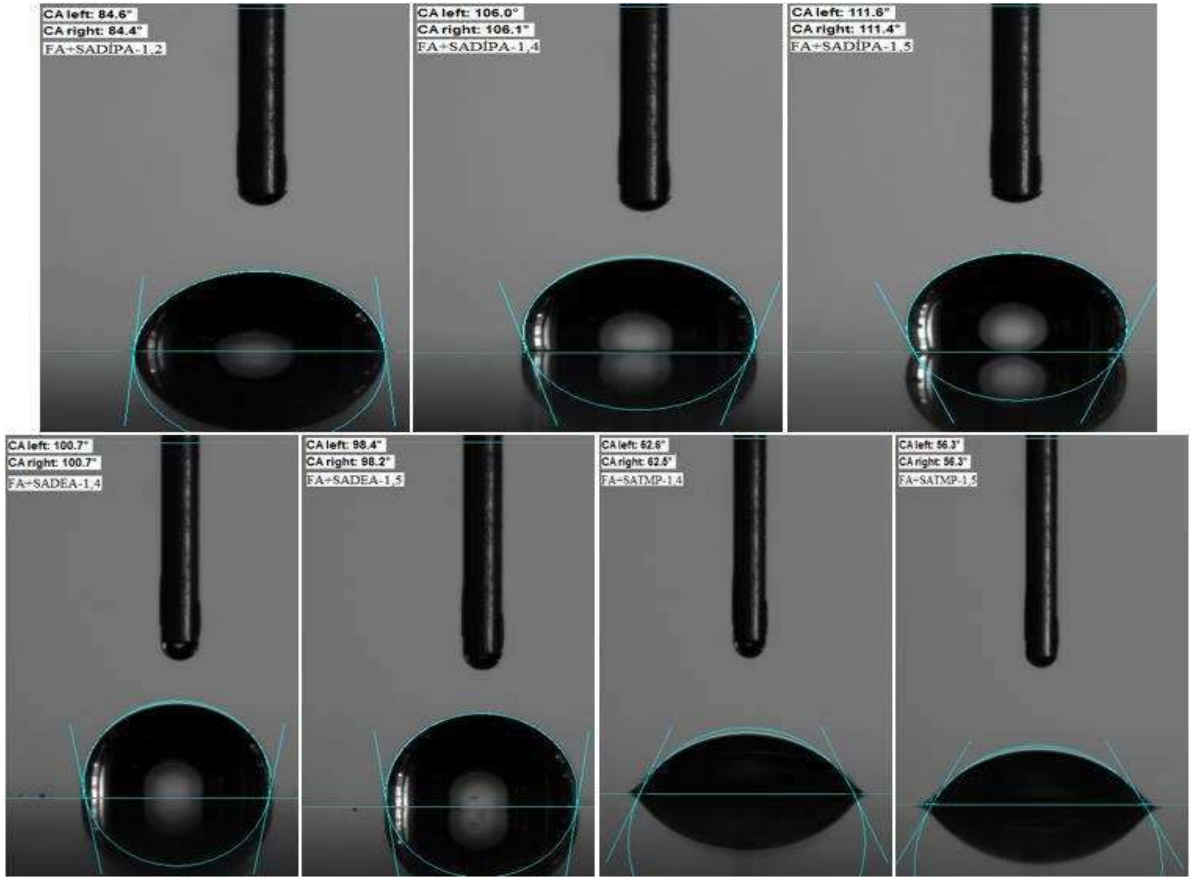


***Note**: Measurements were done with 60% solid content.*

- There is a positive correlation between rheology and molecular weight of the hyperbranched polymers.
- All polymers have behaved as Newtonian fluids except polymers synthesized from SADEA polyol.

4. RESULTS and DISCUSSION

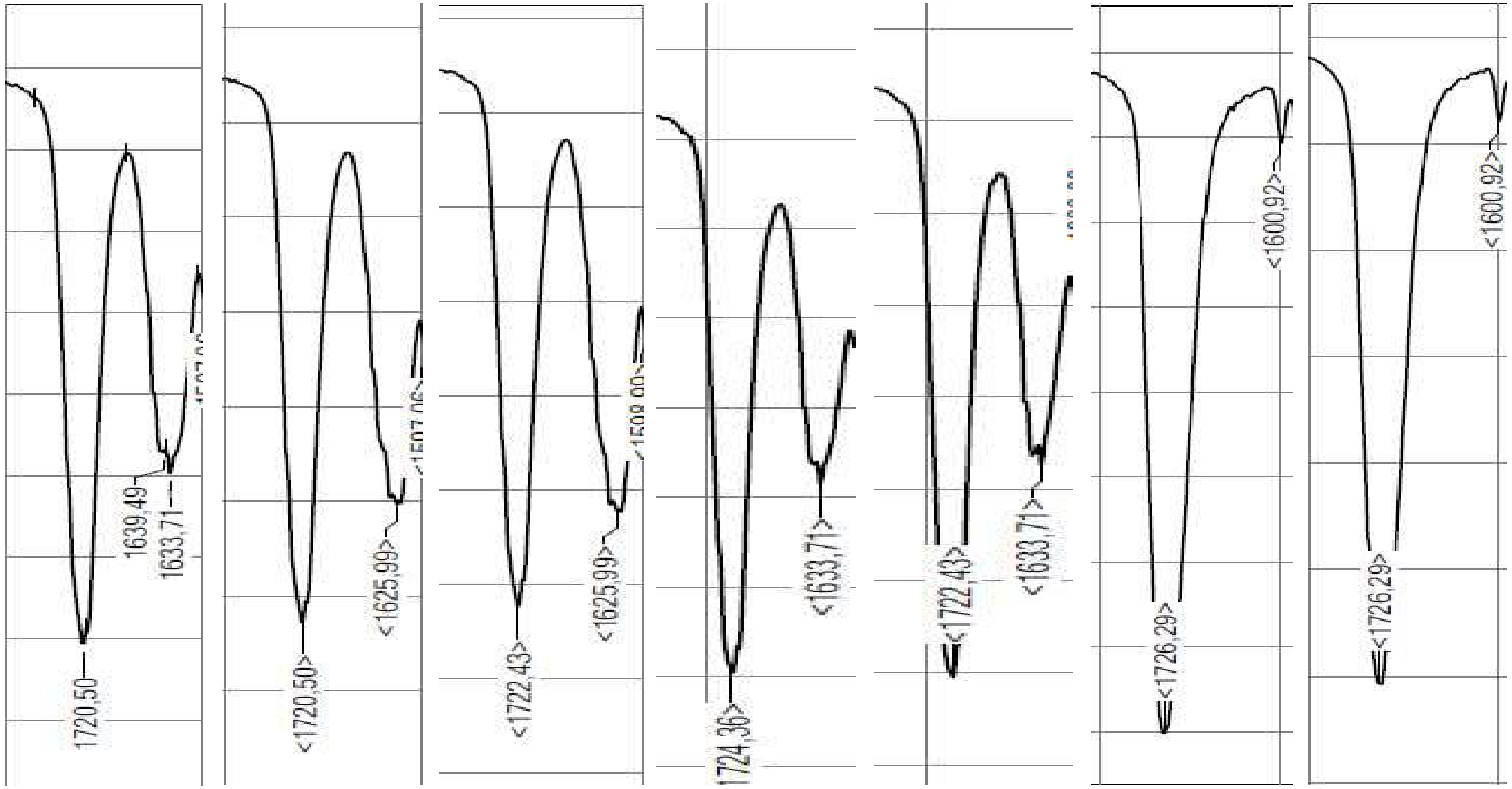
Characterization of Hyperbranched Polymers



Hyperbranched Polymers	Left Contact Angle (°)	Right Contact Angle (°)
FA+SADIPA-1,2	84,6	84,4
FA+SADIPA-1,4	106,0	106,1
FA+SADIPA-1,5	111,6	111,4
FA+SADEA-1,4	100,7	100,7
FA+SADEA-1,5	98,4	98,2
FA+SATMP-1,4	62,6	62,5
FA+SATMP-1,5	56,3	56,3

4. RESULTS and DISCUSSION

Characterization of Hyperbranched Polymers



(a) (b) (c) (d) (e) (f) (g)

(a) FA+SADIPA-1,2 (e) FA+SADEA-1,5
(b) FA+SADIPA-1,4 (f) FA+SATMP-1,4
(c) FA+SADIPA-1,5 (g) FA+SATMP-1,5
(d) FA+SADEA-1,4

Formation of amide and ester bonds was investigated.

Carboxyl group stretching band:
1750 – 1725 cm^{-1} – Saturated aliphatic ester
1740 – 1705 cm^{-1} – Aryl ester

Stretching band of carbonyl group of tertiary amides:
1670 – 1630 cm^{-1}

4. RESULTS and DISCUSSION

Characterization of Hyperbranched Polymers

Hyperbranched Polymers	1st Heating Run		2nd Heating Run		GPC Analysis			^{13}C-NMR Analysis
	T_g-1 (°C)	T_g-2 (°C)	T_g-1 (°C)	T_g-2 (°C)	$\overline{Mn}$ (x10³)	$\overline{Mw}$ (x10³)	PDI	Degree of Branching (%)
FA+SADIPA-1,2	-	-	-4,20	-	3,163	27,070	8,560	76,09
FA+SADIPA-1,4	-	-	-11,25	-	2,987	9,836	3,293	73,91
FA+SADIPA-1,5	-	-	-13,70	18,25	2,856	7,247	2,537	85,61
FA+SADEA-1,4	-17,74	-	-	-	11,960	20,710	1,732	75,05
FA+SADEA-1,5	-18,42	7,01	-	-	10,510	20,040	1,906	82,62
FA+SATMP-1,4	-	-	-38,28	-13,83	2,218	5,536	2,496	86,79
FA+SATMP-1,5	-	-	-39,12	-15,72	2,102	4,402	2,094	89,55

4. RESULTS and DISCUSSION

2K Polyurethane Clear Coat (Varnish) Formulation

Component	VSADIPA-1,2	VSADIPA-1,4	VSADIPA-1,5	VSADEA-1,4	VSADEA-1,5	VSATMP-1,4	VSATMP-1,5
Resin	76,95	76,94	81,13	76,99	73,02	81,10	82,75
Xylene	12,95	12,96	8,77	12,91	16,88	8,80	7,15
n-Butyl Acetate	10,00						
DBTDL	0,1						

Component	Amount (%)
Desmodur Z 4470 MPA/X	22,86
Desmodur N 3600	24,00
n-Butyl Acetate	53,14

Spect.	VSADIPA-1,2	VSADIPA-1,4	VSADIPA-1,5	VSADEA-1,4	VSADEA-1,5	VSATMP-1,4	VSATMP-1,5
Hydroxyl Equivalent Weight (g)	652,83	544,00	505,17	514,38	477,67	545,27	506,33
Isocyanate Equivalent Weight (g)	509,71						
1.Component / 2. Component(g)	1,100/ 1,031	1,023/ 1,151	0,987/ 1,196	0,9999/ 1,189	0,963/ 1,234	1,024/ 1,149	0,988/ 1,194
NCO/OH	1,2005	1,2008	1,2010	1,2000	1,2009	1,2003	1,2005
Solid Content on PU Film (g)	1,0724	1,0742	1,0706	1,0755	1,0714	1,0740	1,0704

4. RESULTS and DISCUSSION

Characterization of Polyurethane Films

Polyurethane Films	1st Heating Run		2nd Heating Run	
	T_g-1 (°C)	T_g-2 (°C)	T_g-1 (°C)	T_g-2 (°C)
PSADIPA-1,2	47,81	-	-	-
PSADIPA-1,4	44,38	-	-	-
PSADIPA-1,5	49,09	-	-	-
PSADEA-1,4	53,01	62,70	-	-
PSADEA-1,5	52,75	62,71	-	-
PSATMP-1,4	42,45	-	-	-
PSATMP-1,5	45,61	-	-	-

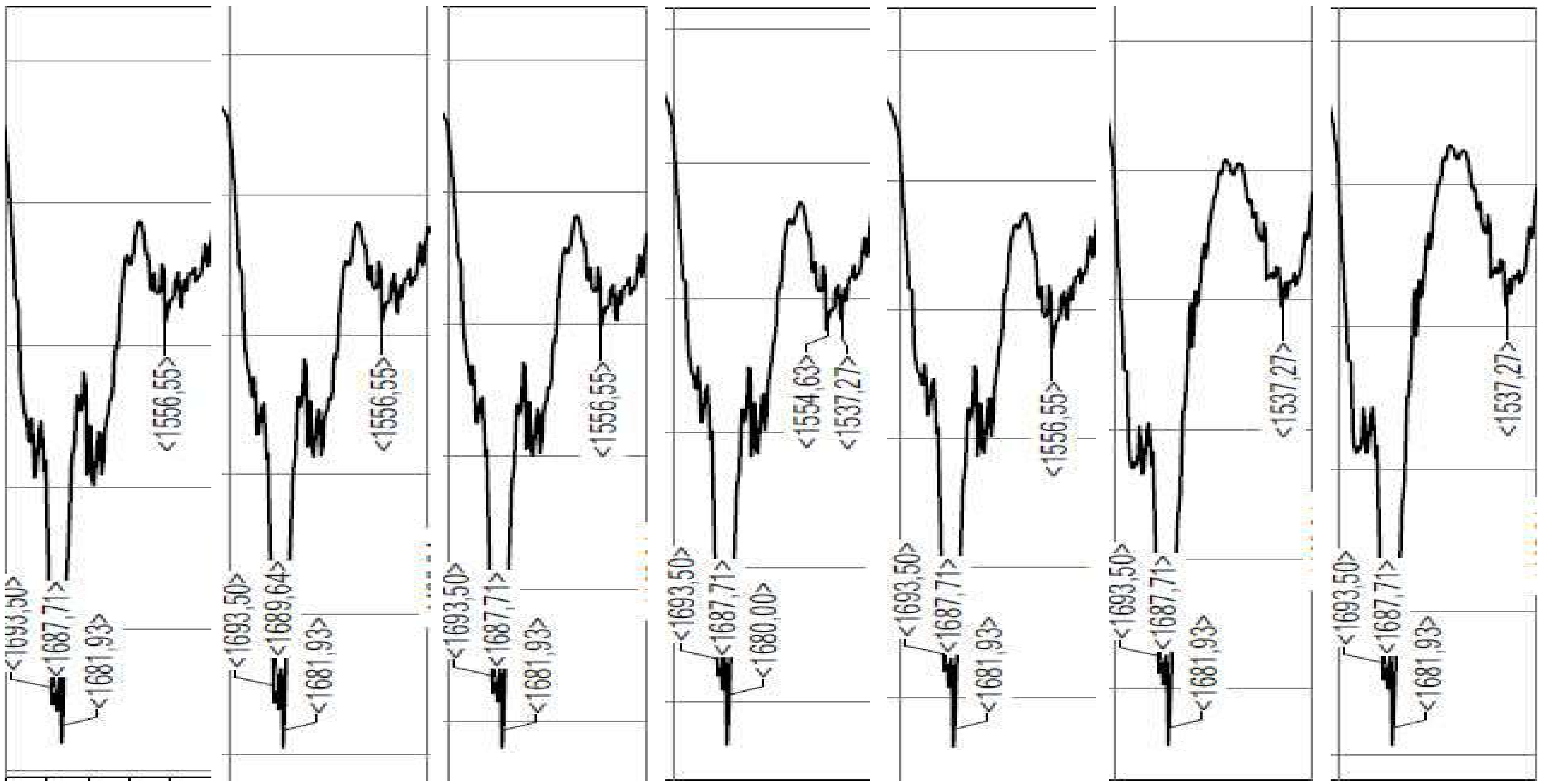
First heating run was taken into account for determination of glass transition temperature of PU films

After the curing process, urethane bonds were formed and glass transition temperature have increased.

Hyperbranched polymer synthesis that contains SADEA polyol, side reactions like cyclization was supposed to be occured and it caused an increase in glass transition temperature.

4. RESULTS and DISCUSSION

Characterization of Polyurethane Films



(a) (b) (c) (d) (e) (f) (g)

(a) PSADIPA-1,2
(b) PSADIPA-1,4
(c) PSADIPA-1,5
(d) PSADEA-1,4
(e) PSADEA-1,5
(f) PSATMP-1,4
(g) PSATMP-1,5

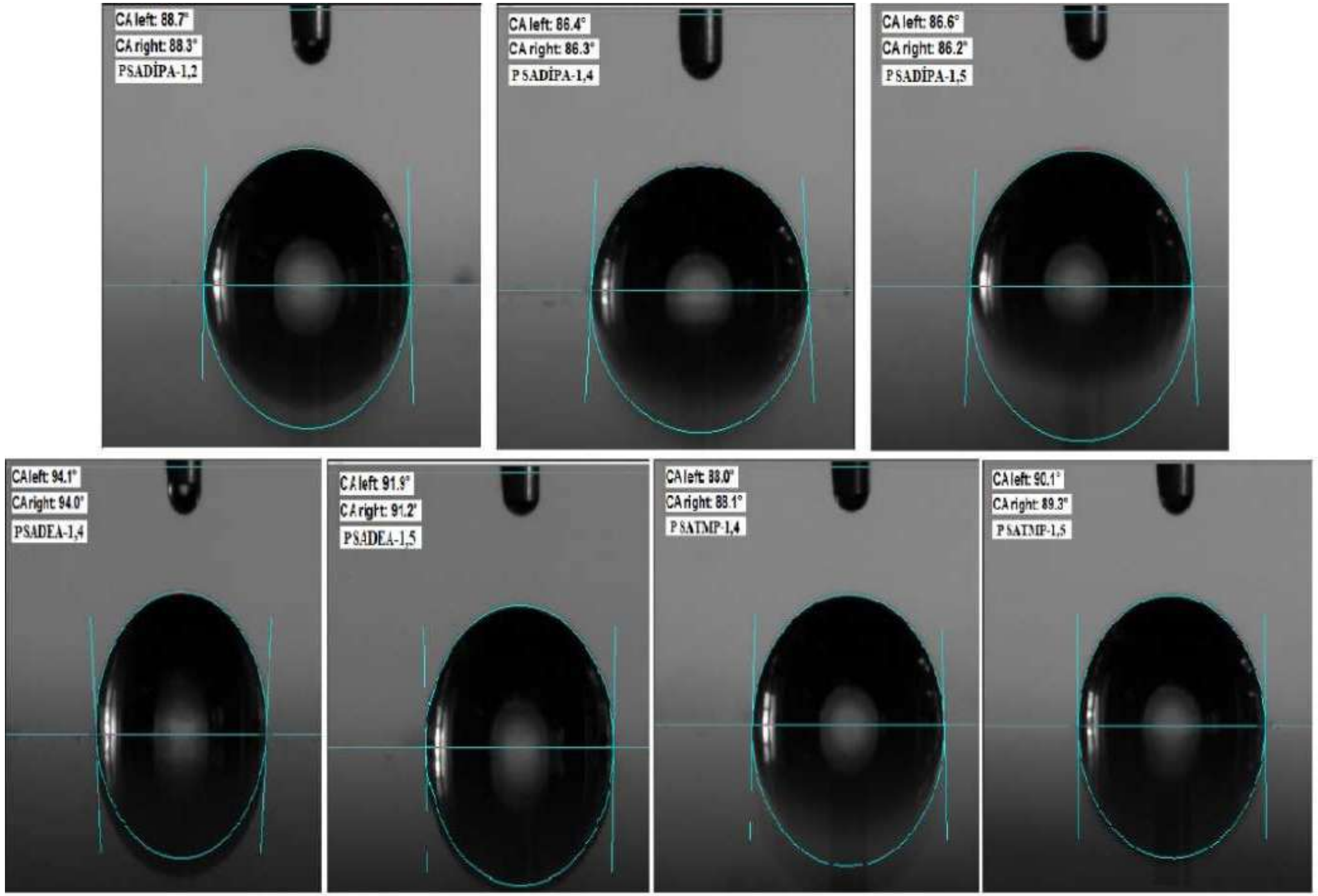
Formation of urethane group was investigated.

Stretching band of C=O group of alkyl urethane: 1740 – 1680 cm^{-1}

N-H deformation and C-N stretching band of secondary urethane: 1600 – 1500 cm^{-1}

4. RESULTS and DISCUSSION

Characterization of Polyurethane Films



Polyurethane Films	Left Contact Angle (°)	Right Contact Angle (°)
PSADIPA-1,2	88,7	88,3
PSADIPA-1,4	86,4	86,3
PSADIPA-1,5	86,6	86,2
PSADEA-1,4	94,1	94,0
PSADEA-1,5	91,9	91,2
PSATMP-1,4	88,0	88,1
PSATMP-1,5	90,1	89,3

4. RESULTS and DISCUSSION

Performance Tests of Polyurethane Films

Polyurethane Films	Drying Time		Gloss	
	Set-to-Touch Time (min.)	Dry-Hard Time (min.)	20°	60°
PSADIPA-1,2	15	290	146	154
PSADIPA-1,4	15	312	158	159
PSADIPA-1,5	20	340	147	153
PSADEA-1,4	15	82	11,7	37,4
PSADEA-1,5	15	94	10,6	34,4
PSATMP-1,4	15	360	155	157
PSATMP-1,5	14	373	158	159

Set-to-touch time of PU films are similar.

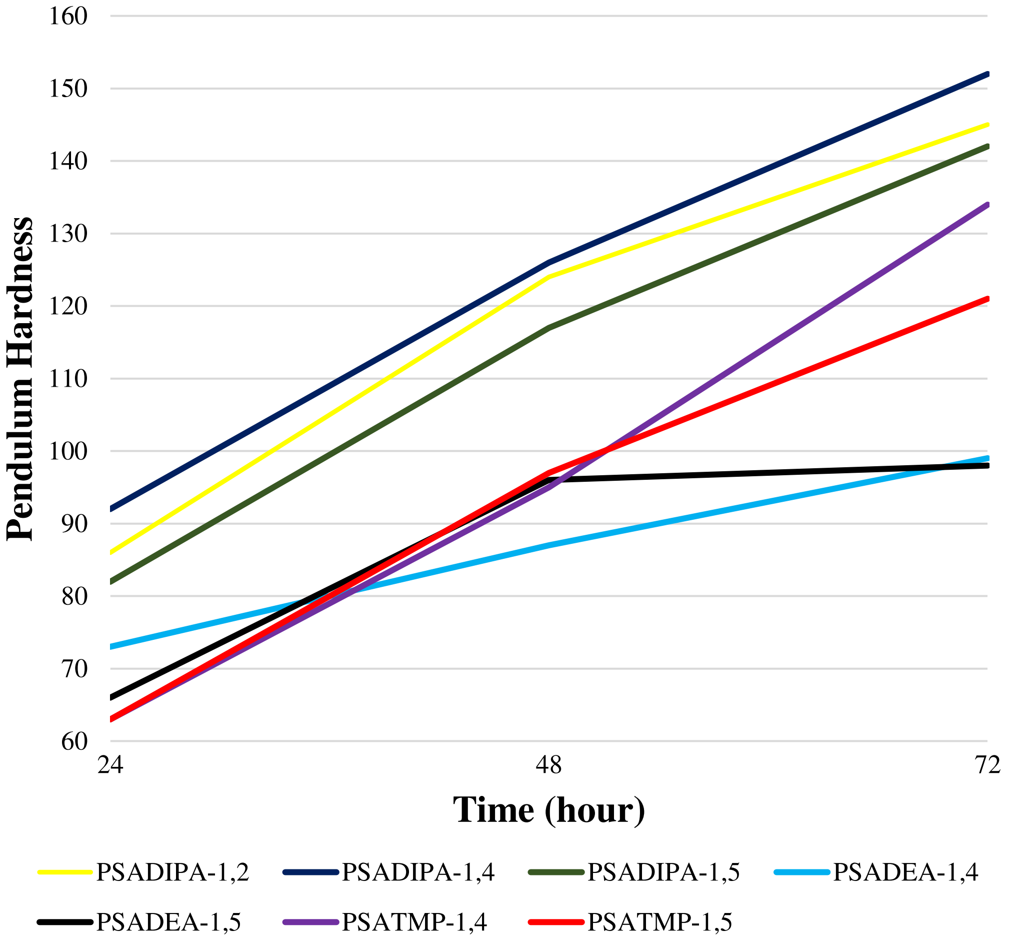
Dry-hard time of the films inversely proportional to the molecular weight of the hyperbranched polymers

PU films prepared by using SADEA polyol was matt due to incompatability between hyperbranched polymer and polyisocyanate oligomer.

4. RESULTS and DISCUSSION

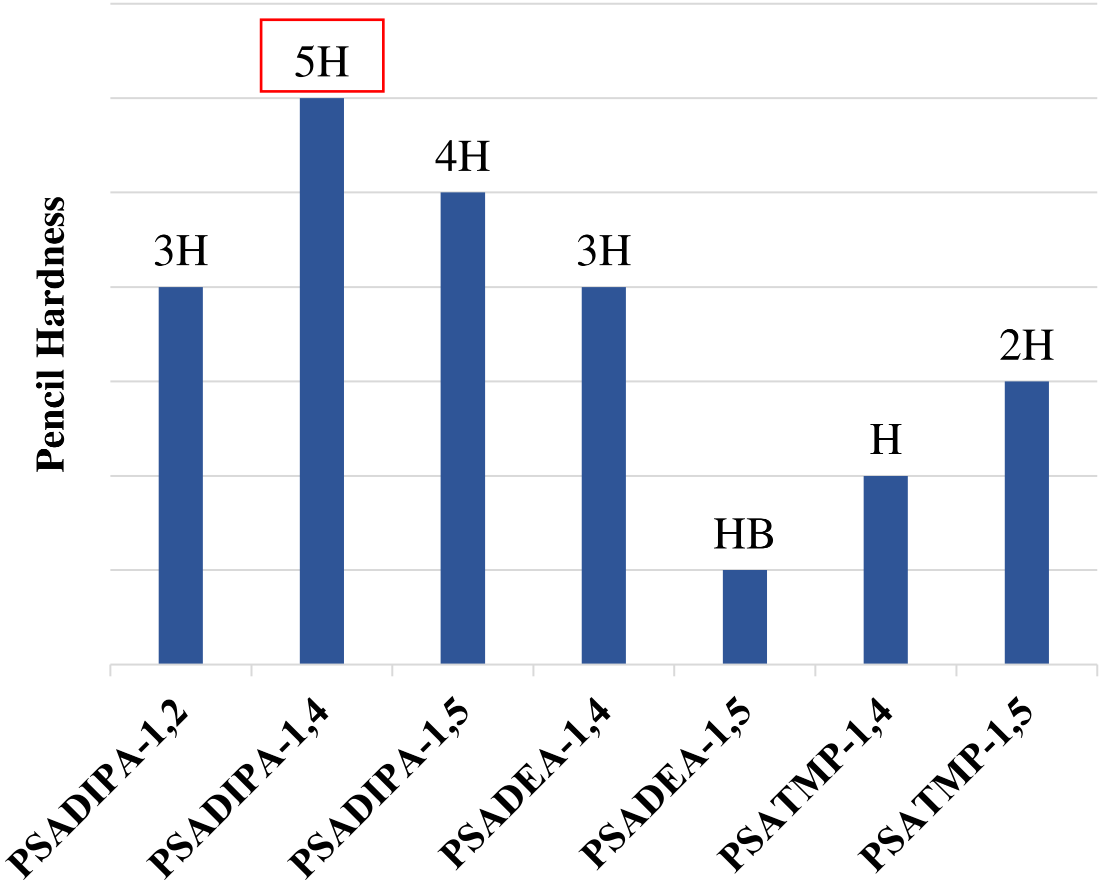
Performance Tests of Polyurethane Films

Polyurethane Films	Konig Pendulum Hardness		
	24 Hours	48 Hours	72 Hours
PSADIPA-1,2	86	124	145
PSADIPA-1,4	92	126	152
PSADIPA-1,5	82	117	142
PSADEA-1,4	73	87	96
PSADEA-1,5	66	97	95
PSATMP-1,4	63	95	134
PSATMP-1,5	63	97	121



4. RESULTS and DISCUSSION

Performance Tests of Polyurethane Films

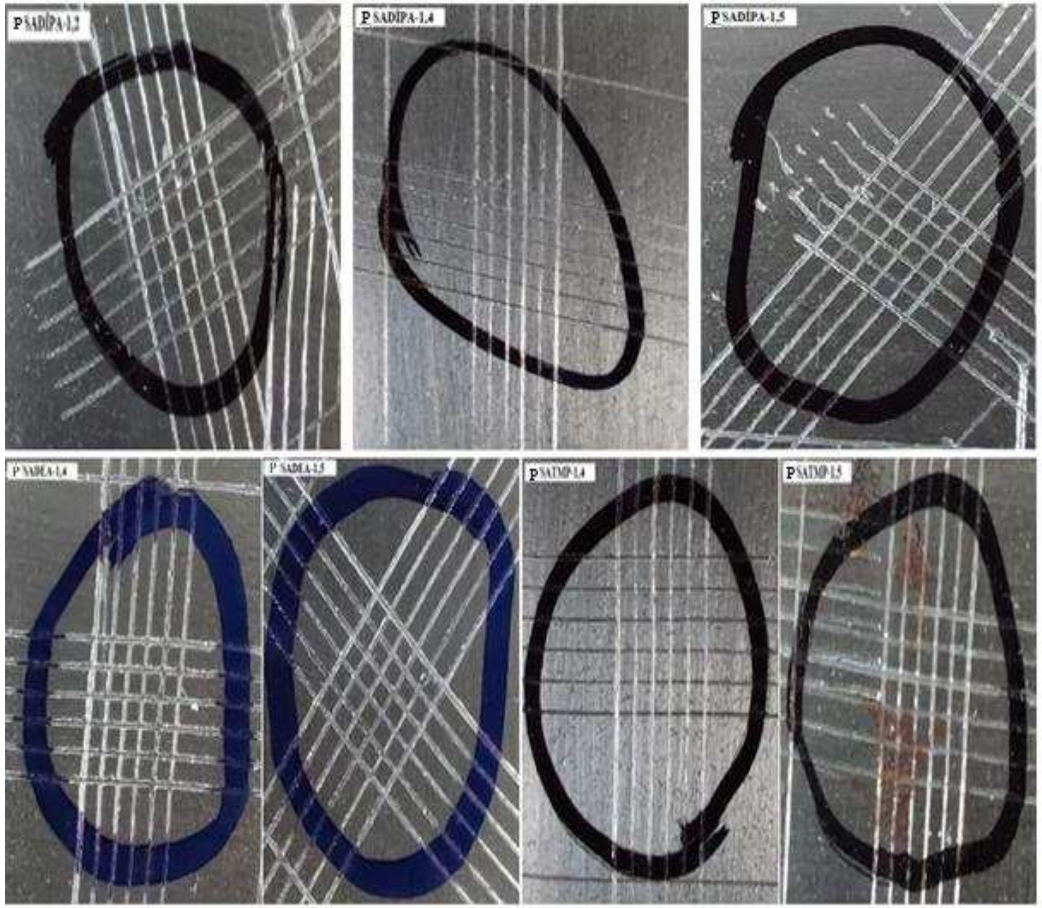


Polyurethane Films	Dry Film (mg)	Insoluble Film (mg)	Gel Content (%)
PSADIPA-1,2	49,5	48,6	98,18
PSADIPA-1,4	54,1	53,9	99,63
PSADIPA-1,5	60,6	59,9	98,84
PSADEA-1,4	48,5	46,1	95,05
PSADEA-1,5	48,3	47,7	98,76
PSATMP-1,4	56,5	51,5	91,15
PSATMP-1,5	57,6	53,8	93,40

4. RESULTS and DISCUSSION

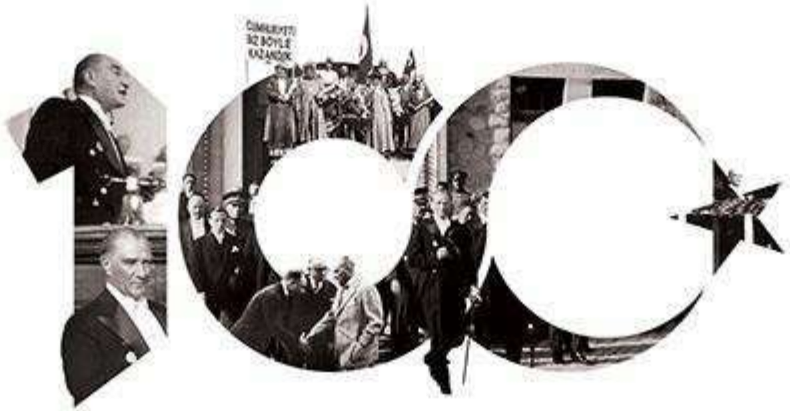
Performance Tests of Polyurethane Films

Polyurethane Films	Impact Resistance (kg x cm)	Bending Test	Dry Film Thickness ($\mu m \pm 2$)
PSADIPA-1,2	72	Pass	7
PSADIPA-1,4	72	Pass	5
PSADIPA-1,5	72	Pass	3
PSADEA-1,4	36	Pass	23
PSADEA-1,5	27	Pass	17
PSATMP-1,4	72	Pass	5
PSATMP-1,5	72	Pass	25



5. CONCLUSIONS

1. Amide and ester functional biobased polyols and hyperbranched polymers were successfully synthesized.
2. Reactivity of hydroxyl groups on dialkanol amines was directly affected the course of reaction.
3. Amide groups have increased thermal, thermo-oxidative and scratch resistance of polyurethane films.
4. It was concluded that there is a positive correlation between scratch resistance and gel content of the polyurethane film.
5. Synthesized polymers have showed Newtonian behaviour that is a proof of hyperbranched structure.
6. In this study, biobased hyperbranched polymers that have similar performance with commercial products were synthesized by using commercially available raw materials. Therefore it is suitable for scale-up.



THANK YOU !

Hayatta en hakiki mürşit ilimdir.

Our true mentor in life is science.