Erzincan Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
2021, 14(3), 1077-1086
ISSN: 1307-9085, e-ISSN: 2149-4584
Araştırma Makalesi

Erzincan University
Journal of Science and Technology
2021, 14(3),1077-1086
DOI:10.18185/erzifbed. 948029
Research Article

The Identification and Characterization of Unsaturated Polyester Resins Used in the Coating Industry

Ayça Biçen*, Nazlı Güvenç

Kansai Altan Boya Sanayi ve Ticaret A.Ş. Ankara Asfaltı 25.km - 35730 Kemalpaşa, Izmir

Geliş / Received: 04/06/2021, Kabul / Accepted: 31/07/2021

Abstract

Unsaturated polyester resins (UPRs) are chemical structures, consisting of relatively short polyester chains that are cross-linked by longer chains of vinylic material such as styrene. Saturated and unsaturated components are mostly composed of phthalic acid and maleic anhydride. Furthermore, vinyl monomers and diols constitute the structure of UPRs. As a consequence, a variety of diols and acids might be used for the polymerization of unsaturated polyesters depending on properties desired for the final product. The identification of degradation products of UPRs is of significance to investigate different properties of unsaturated polyesters as a result of their structures. Gas chromatography with Mass Spectroscopy equipped with pyrolysis provides an important technique for the identification and characterization of UPRs. In this study, initially the UPRs were analyzed with Fourier Transform Infrared Spectroscopy (FT-IR) to characterize the specific peaks that belong to UPRs. Afterwards, all anhydride, acid and diol groups participating in the structure of different UPRs were characterized by Pyr-GC/MS method. Degradation products of each resin were characterized and the obtained results were compared with monomer references. In addition, a special reaction mechanism was observed between cyclopentadiene and dimethyl maleate that forms dimethyl-5-cis-norbornene-2-3-dicarboxylic acid due to methylation process as a sampling method. These findings might lead to the development of unsaturated polyester resins with different types of monomers and properties in the coating industry.

Keywords: Unsaturated Polyester resin, Pyrolysis-GCMS, FT-IR, Characterization, Organic Coating.

Boya Endüstrisinde Kullanılan Doymamış Polyester Reçinelerin Belirlenmesi ve Karakterizasyonu

Öz

Doymamış polyester reçineleri (UPR'ler), stiren gibi daha uzun vinil yapılı malzeme zincirleriyle çapraz bağlanmış nispeten kısa polyester zincirlerinden oluşan kimyasal yapılardır. Doymuş ve doymamış bileşenler çoğunlukla sırasıyla ftalik asit ve maleik anhidrit monomerlerinden oluşur. Ayrıca, vinil monomerler ve dioller, UPR'lerin yapısını oluşturur. Sonuç olarak, son ürün için istenen özelliklere bağlı olarak doymamış polyesterlerin polimerizasyonu için çeşitli dioller ve asitler kullanılabilir. UPR'lerin bozunma ürünlerinin belirlenmesi, doymamış polyesterlerin yapılarının bir sonucu olarak farklı özelliklerini araştırmak için önemlidir. Piroliz ile kombinlenmiş gaz kromatografisi - kütle spektrometresi (Pyr-GC/MS), UPR'lerin belirlenmesi ve karakterizasyonunda için önemli bir role sahiptir. Bu çalışmada, başlangıçta UPR'ler, UPR'lere ait spesifik pikleri karakterize etmek için Fourier Dönüşümü Kızılötesi Spektroskopisi (FT-IR) ile analiz edildi. Ardından, farklı UPR'lerin yapılarındaki tüm anhidrit, asit ve diol grupları Pyr-GC/MS yöntemi ile karakterize edilmiştir. Her reçinenin bozunma ürünleri karakterize edilmiş olup, elde edilen sonuçlar monomer referansları ile karşılaştırıldı. Ayrıca, metilasyon işlemi ile örnekleme sırasında siklopentadien ile dimetil maleat arasında dimetil-5-cis-norbornen-2-3-dikarboksilik asit yapısını oluşturan olarak özel bir reaksiyon mekanizması gözlemlendi. Bu bulgular, boya endüstrisinde farklı tipte monomerlere ve özelliklere sahip doymamış polyester reçinelerinin geliştirilmesine katkı sağlayabilir.

Anahtar kelimeler: Doymamış Polyester Reçineleri, Piroliz-GCMS, FT-IR, Karakterizasyon, Organik Kaplama.

---

*Corresponding Author: ayca.bicen@kansaialtan.com.tr

1. Introduction

Polyesters are one of the most comprehensive synthetic copolymers and classified into two main groups, saturated (SPRs) and unsaturated polyester resins (UPRs). SPRs are formed by the reaction of polybasic acids and polyols, and do not contain double bonds in their main chain whereas UPRs contain double bonds in their main chain. Generally, UPRs are produced from inexpensive monomers and through an easy synthesis process which offers advantages of light weight, high strength and excellent mechanical properties. Consequently, they have significantly attracted the attention of the academia and the industry in a wide range of applications such as fibers, plastics, composites and coating applications (R. Alabbas et al.,2017)

Unsaturated polyesters are the third-largest class of thermoset molding resins, they are produced by the condensation of a diol with a blend of saturated and unsaturated anhydrides. Recently, several researches have been conducted on the reaction mechanism of UPRs. The reaction occurs as a result of free-radical chain-growth copolymerization of unsaturated sites that are present in the polyester backbone with the styrene monomer that functions as an agent and solvent to form linkage between the two unsaturated polyester molecules.

Besides, polyesters are heterochain macromolecules with carboxylate ester groups at their polymer backbones. The properties of cross-linked resin depend on the types and amounts of anhydrides and glycols used for polymerization. Commonly, the resulting UPRs consist of phthalic acid and maleic anhydride as a blend of saturated and unsaturated anhydrides. Moreover, 1, 2-propylene glycol is often used as the diol in the polymer and the condensation of these products forms a cross-link with styrene as a reactive vinyl monomer (Y.S. Yang and L.J. Lee,1988).

Different glycols, acids and anhydrides might be used for the polymerization of UPRs to acquire the desired properties. For instance, isophthalic acid (IPA) and terephthalic acid (TPA) might be used to achieve thermal and chemical resistance. On the other hand, adipic or succinic acid might improve the flexibility of the final product yet reduce the thermal and chemical resistances. These parameters influence the reactivity of the curing agent and the mechanical properties of the final product. Thus, the choice of the monomer types and their amounts are very substantial for the desired product. Briefly, the characterization of UPRs are complex and special identification studies are required to investigate the entire structure of UPRs (J.H. Aurer and A. Kasper,2003).

In this study, sensitive techniques are used to characterize the components of coating systems such as Fourier Transform Infrared (FT-IR) and Pyrolysis-Gas Chromatography with Mass Spectrometry (Py-GC/MS). FT-IR is a sufficient method for the characterization of very complex mixtures whereas Py-GC/MS is convenient to analyze the composition of polymers such as UPRs, investigate the degradation of resin materials, and separate their monomers qualitatively and quantitatively. This method has different pre-treatment processes such as direct injection and chemical derivatization before injection, based on the compound types. Tetramethyl-ammonium hydroxide (TMAH) is commonly used as a derivatizing agent before pyrolysis for the elucidation of the structure of UPRs to identify their monomer types by methylation (Ma et al.,2014 and R.A. Parıldar and A. Biçen,2012).

The aim of the study is to analyze UPRs via identification and characterization of all anhydrides, acid and diol groups, to determine the interaction of certain additives with resin and possible side reactions by using Pyr-GC/MS.

2. Materials and Methods

As given in Table 1, UPR1, UPR2, UPR3 and UPR4 resins that contain different diols and dibasic acids were cooked for characterization and identification of degradation products of the resin materials. In general, maleic anhydride serves C=C double bonds to the polyester resin, and polyol groups and acids act as chain extenders. The aromatic ring structure of isophthalic acid makes the chain more rigid and more compatible with styrene monomer. After FT-IR spectra was collected for each synthesized resin, the combination of Pyrolysis and Gas Chromatography/Mass Spectrometry techniques was used for polymer characterization. For the sampling of Pyr-GC/MS analysis, each 0.25 g resin was treated with 3 ml TMAH for methylation and 3 ml THF as a solvent for 45 min at 250-300 °C, in order to derive the monomers of the resin in their volatile form. When methylation was achieved, resins were placed into sample tubes filled with glass wool that hold the resins in the pyrolysis chamber for degradation of the resin into its monomers.

Table 1. Contents of resins that are used for characterization. The monomers used for each resin are indicated by the '+' sign and '–'sign is used for unused monomers for each resin.

	***Resin Contents**											
	Unsaturated Acid/Anhydride Types	**Saturated Acid/Anhydride Types**					**Polyol Group Types**					**Vinyl Monomer**
	MA	**PA**	**IPA**	**AA**	**BA**	**SA**	**NPG**	**MPG**	**MEG**	**MDG**	**TCDM**	**St**
UPR1	+	-	-	-	-	-	-	-	+	+	-	+
UPR2	+	-	-	-	-	-	-	+	-	-	-	+
UPR3	+	+	-	+	+	-	-	-	-	-	+	+
UPR4	+	-	+	+	+	+	+	-	-	-	-	+

***Monomers Selection.** Maleic Anhydride (MA), Phthalic Anhydride (PA), Isophthalic Anhydride (IPA), Benzoic Acid (BA), Adipic Acid (AA), Succinic Acid (SA), Neopentyl Glycol (NPG), Monopropylene Glycol (MPG), Monoethylene Glycol (MEG), Monodiethylene Glycol (MDG) and Tricyclodecane dimethanol (TCDM) were used in this study since they are commonly used monomers in the paint industry.

2.1. FT-IR Analysis

FT-IR attached to Attenuated Total Reflectance (ATR) was used for the characterization of polymeric structures and KBr pellet was used for the identification of fingerprint region of polymeric material. The chemical structure of the UPRs were investigated by FT-IR Spectroscopy (Perkin Elmer Spectrum One) with the parameters shown in Table 2.

Table 2. FT-IR Parameters

FT-IR (Perkin Elmer Spectrum One)	
Wavelength	4000 cm^{-1} to 450 cm^{-1}
Resolution	4 cm^{-1}
Sampling Technique	KBr pellet

2.2. Pyr-GC/MS Analysis

Analytical Pyrolysis is a technique used for the characterization of a material through chemical degradation reactions induced by thermal energy; the volatile pyrolysates are separated and analyzed by GC/MS. In order to obtain acids and diols of polyester monomers, chemical derivatization by using TMAH (Tetramethylammonium Hydroxide) as a thermally assisted hydrolysis and methylation (THM) technique, was optimized**.** Optimized GC/MS method for the seperation of monomers is summarized in Table 3.

Table 3. Pyr-GCMS Parameters

GCMS (Thermo-1310)	
Inlet	320°C
GC Method	Combined with varying the oven temperature ramp rate
Column	5 % Phenyl – methylpolysiloxane
Carrier Gas	He
Pyrolyzer (CDS-5250)	
Valve Oven	300°C
Transfer Liner	350°C
Pyrolyzer	750°C
Pyrolysis time	30 second

3. Results and discussion

3.1. FT-IR Characterization

Fourier Transform Infrared Spectrophotometry (FT-IR) provides a quick and relatively inexpensive method for the identification and characterization of resin types and occasionally provides semi-quantitative results. In this study, FT-IR was used to identify the UPRs to provide specific characterization before Pyr-GC/MS analysis. The spectrums of UPRs, characterized by FT-IR spectroscopy are shown in Figure 1. The spectra of the UPRs show bands at 1645 and 1520 cm^{-1} characteristic for the double bond from the maleic structure and bands for the valence vibration of the OH groups at 3378 cm-1, and the carbonyl group at 1727 cm^{-1}. The other bands are localized at 2877 cm^{-1} (CH2 group) and 2819 cm^{-1} (CH3 group), respectively. All resins (UPR1, UPR2, UPR3 and UPR4) were derivatized with tetramethylammonium hydroxide (TMAH) in order to obtain methyl ester groups to be analyzed by PYR-GC/MS. The derivatization products were injected to the PYR-GC/MS and all peaks were defined by the Wiley Library of MS spectrum.

The characteristic peaks were determined for all monomer structures. In Figure 2, full chromatograms of each resin are shown. All acid and diol types that constitute the UPRs were successfully identified. According to the chromatogram of the UPR1, Monoethylene Glycol (MEG) and Monodiethylene Glycol (MDG) served as diol types in the resin, characteristic peaks were detected at retention time of 2.06 and 11.63 minute, respectively. For UPR2, the characteristic peaks of Monopropylene Glycol (MPG) were detected at the beginning of the chromatogram whereas Neopentyl Glycol were found at retention time of 8.69 minute.

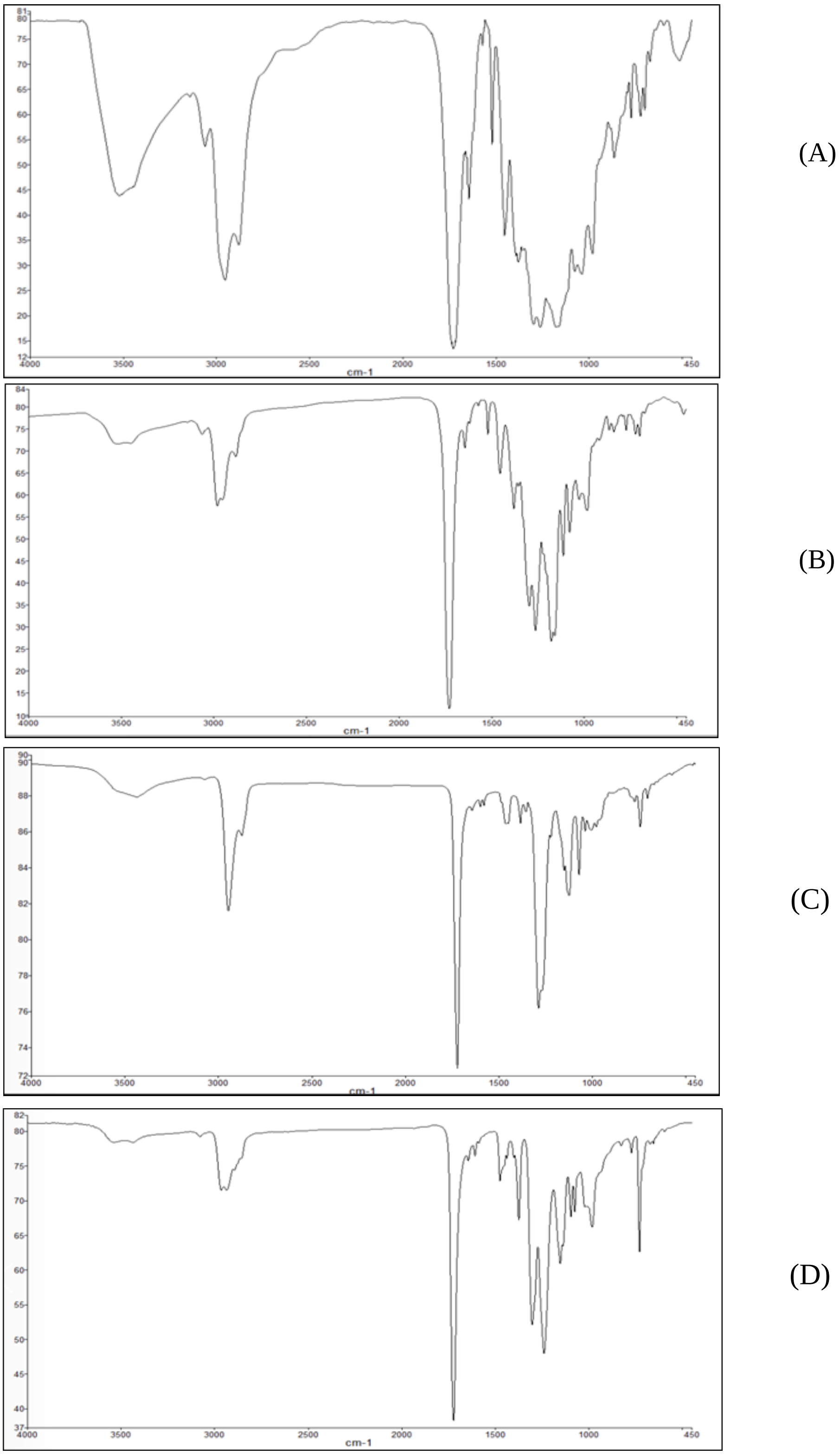

Figure 1. FT-IR spectrum of UPR1 (A), UPR2 (B), UPR3 (C) and UPR4 (D), respectively.

3.2. Pyr- GC/MS Characterization

In addition, maleic anhydride characterization was essential for all resins. Maleic anhydride was detected at retention time of 13.93 minute and named as a dimethyl fumarate for methyl ester form of maleic anhydride from the Wiley Library search. Since maleic acid has an isomer structure named as fumaric acid, it is predictable that library search gives this result for maleic anhydride. However, while maleic acid has the anhydride form, fumaric acid does not. Consequently, both types of characterization of acids and diols played a critical role for the understanding of the components of UPRs. In order to undergo methylation process, neither acids and anhydrides nor diols reveal themselves as they are. For this reason, each monomer type detected with MS library were injected to Pyr-GC/MS system as a reference to check the identification during characterization of the resins. After comparing and matching each reference with the component of each resin, characterizations were concluded, and results are shown in Table 4.

Table 4. Characterization of monomers by Pyr-GC/MS after methylation.

Reactant Name	CAS No	Retention Time (GC/MS)	Degradation Product	MS Spectrum Product(m/z)
Phthalic Anhydride (PA)	85-44-9	18.60	Methyl Phthalate	163.08-77.09
Isophthalic Anhydride	1459-93-4	18.97	Dimethyl Isophthalate	163.05- 135.06-194.12-76.07
Maleic Anhydride (MA)	108-31-6	13.04-13.93	Mehyl Fumarate	113.06- 85.04- 59.05
Adipic Acid (AA)	124-04-9	16.94	Dimethyl Adipate	59.04+114.11+143.09+74.05+115.13
Benzoic Acid (BA)	65-85-0	15.24	Methyl Benzoate	105.07-77.08-136.09-51.08
Succinic Acid (SA)	108-30-5	14.13-14.79	Dimethyl 2-methoxysuccinate	75.08-117.10-45.09
Monoethylene Glycol (MEG)	107-21-1	2.40-2.65	2-Methoxyethanol +1.2-Dimethoxyethane	45.10
Monopropylene Glycol (MPG)	57-55-6	2.71-3.15	1-Methoxy-2-propoxy ethane + 3-Methoxybutan-2-ol	45.09+47.09+59.06
Neopentyl Glycol (NPG)	126-30-7	8.69	Neopentanediol	56.10+57.11+45.06+73.10+87.13
, Monodiethylene Glycol (MDG)	111-46-6	11.63	Dowanol DM	45.08+59.11+90.13
Tricyclodecane dimethonanol (TCDM)	26896-48-0	20.27	Tricyclodecane dimethonanol	147.17+119.13+81.13+160.18+120.15+80.64

In Table 4**,** all acid and diol types that compose UPR1, UPR2, UPR3 and UPR4 sample resins are shown with their characteristic peaks and degradation structures.

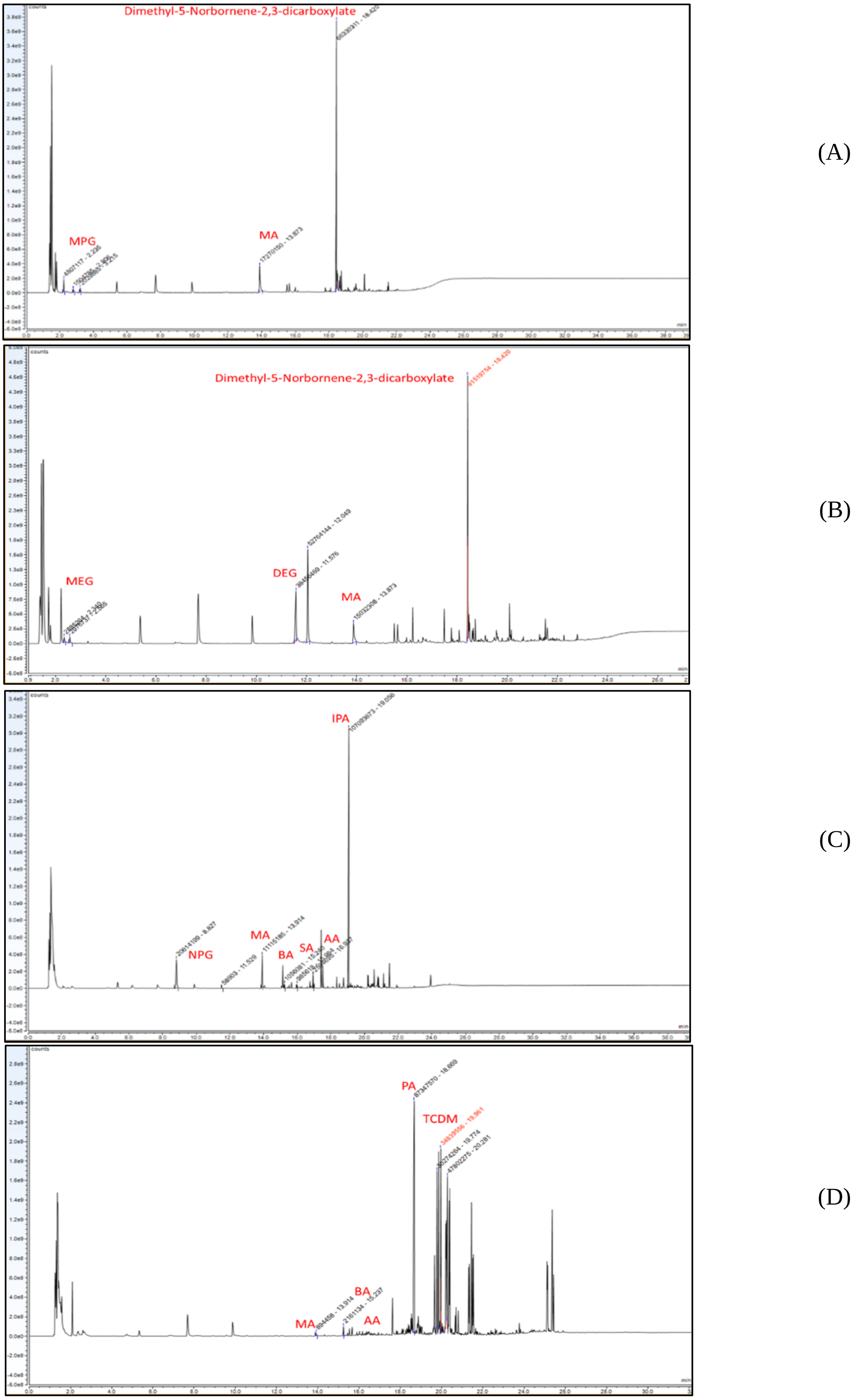

Figure 2. Pyr-GC/MS chromatograms of each resin (UPR1 (A), UPR2 (B), UPR3 (C) and UPR4 (D), respectively)

Besides, a peak with the highest intensity on the chromatograms of UPR1 and UPR2 was observed, it was not a kind of structure that participates in the structure of unsaturated polyester resins. This molecule was defined as Dimethyl-5-Norbornene-2, 3-Dicarboxylate and its characteristic peak was determined at 18.42 as shown in Figure 3a and 3b.

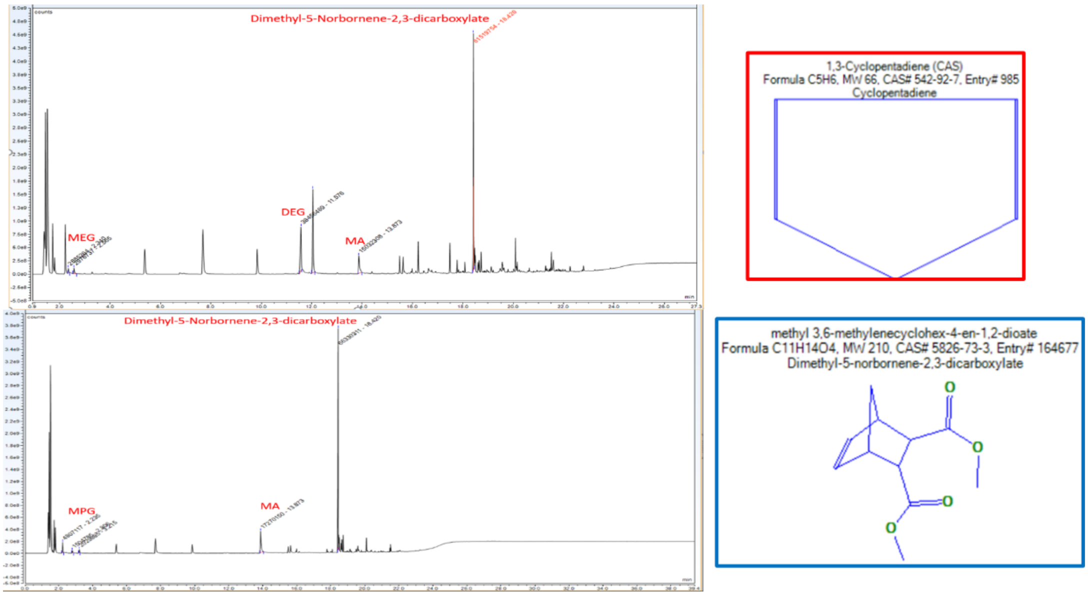

Figure 3a. Overlay chromatogram of UPR1 and UPR2 for the identification of Dimethyl-5-Norbornene-2, 3-Dicarboxylate.

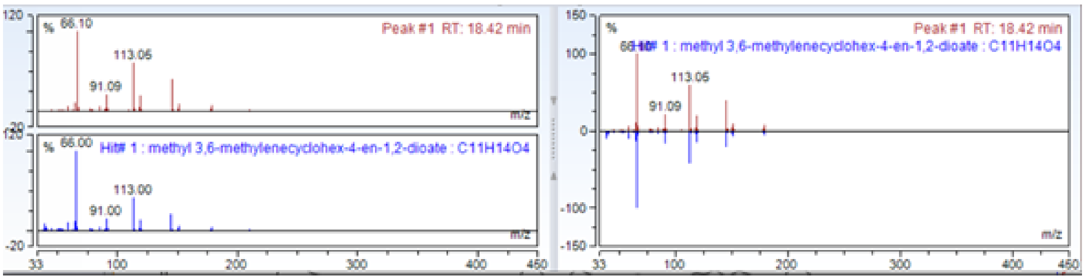

Figure 3b. MS Library identification of Dimethyl-5-Norbornene-2, 3-Dicarboxylate.

When the source of this foreign structure seen in the chromatogram was examined, Dimethyl-5-Norbornene-2,3-Dicarboxylate was observed to appear in the presence of cyclopentadiene. Dicyclopentadiene (DCPD) is a raw material used for the synthesis of UPRs to increase thermal resistance and provide better surface quality of the final product. Further, it can be converted to cyclopentadiene, its monomeric form, which reacts with the double bond of maleic anhydride via Diels-Alder addition. As given in Figure 4, after this reaction, intermediates can be further esterified (polymerized) with a diol such as propylene glycol and might form Dimethyl-5-Norbornene-2, 3-Dicarboxylate at the end.

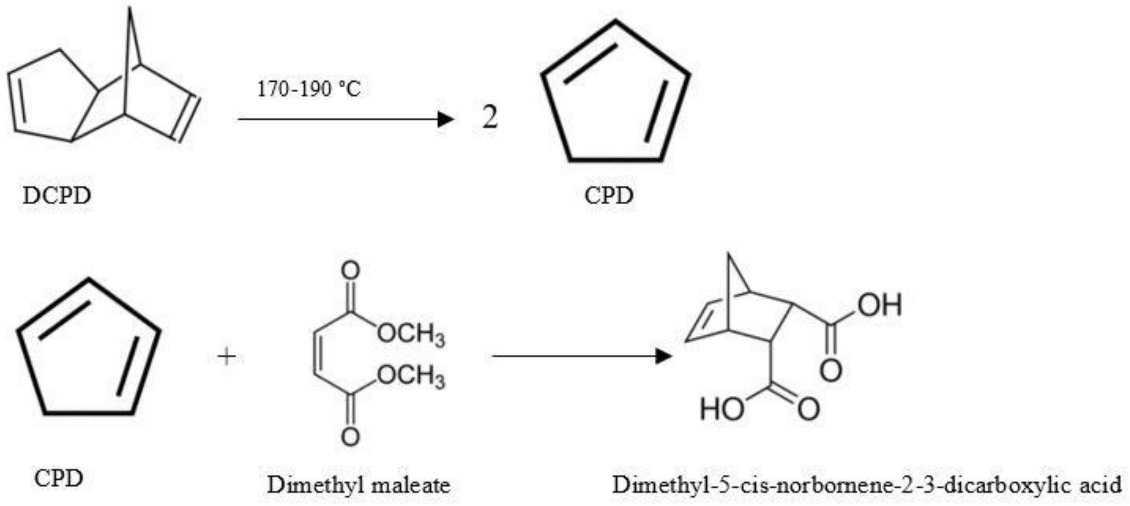

Figure 4. The conversion of DCPD into CPD(top) and the reaction of the CPD into the polymer backbone by means of a reaction with dimethyl maleate (bottom).

4. Conclusions

In conclusion, different types of UPRs were analyzed with both FT-IR and Pyr-GC/MS techniques. The structure of the specific pyrolysis products of unsaturated polymers were obtained by mass spectrometry and characteristic pyrolysis products that discriminate maleic anhydride in the UPRs were determined. All diols and dibasic acids were successfully characterized using both MS library and their references. After the analysis of the structure of specific pyrolysis products, the special reaction mechanism was observed between cyclopentadiene and dimethyl maleate to form dimethyl-5-cis-norbornene-2-3-dicarboxylic acid. These results might be promising to guide the identification and characterization of UPRs and assessment of DCPD usage as an additive in the coating industry.

Acknowledgements

The authors are grateful to Kansai Altan Boya Sanayi ve Ticaret A.Ş., for their support during this work.

References

R.Alabbas, W. Khalil, S. Alhariry (2017), Synthesis and Characterization of Unsaturated Polyester Resin and Studiying Their Thermo Properties, Chemistry and Metarials Research.

Y.S. Yang and L.J. Lee (1988), Microstructure Formation in the Cure of Unsaturated Polyester Resins, Polymer.

J.H. Aurer and A. Kasper (2003), Unsaturated Polyester Resins,Polymers with unlimited possibilities, Die Bibliothek der Technik.

Ma et al. (2014), Application of Pyrolysis Gas Chromatography/Mass Spectrometry in Lacquer Research: A Review, Polymers.

R.A. Parıldar and A.Biçen (2012), Characterization of tertiary amine and epoxy functional all-acrylic coating system, Progress in Organic Coatings