

## 소르빅산 변성 수소첨가 DCPD계 석유수지의 합성 및 응용

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## Synthesis and Application of Sorbic Acid Grafted Hydrogenated Dicyclopentadiene Hydrocarbon Resin

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석유수지는 분자량이 작고 무정형인 열가소성 수지로서 다양한 접착제 및 고무의 가공조제, 필름의 첨가제 등으로 사용되고 있다. 석유수지의 단점은 비극성이기 때문에 비극성의 폴리머와의 상용성은 우수하나 아크릴 및 우레탄, 폴리아마이드와 같은 극성기를 포함하는 폴리머와의 상용성은 좋지 않다. 그뿐만 아니라, 최근 석유수지의 원료로 사용되는 나프타 크래킹 공정에서 나오는 부산물의 양이 가스 크래킹의 확대 적용으로 인해 줄어들고 있는 상황이다. 이러한 문제를 해결하기 위해 본 연구에서는 석유수지 원료로 극성기를 포함하면서 지속 가능한 신규 원료인 소르빅산으로 일부 대체하고자 하였다. 기존 석유수지 원료인 DCPD 모노머와 블루베리로부터 생성되는 소르빅산은 열중합에 의해 Diels-Alder 반응으로 성공적으로 공중합하였다. 소르빅산 변성 수소첨가 DCPD계 석유수지는 아크릴계 접착제 배합에 적용되어 다양한 점·접착 물성이 측정되었으며, Polarity에 따른 상용성 및 연화점에 따라 최적 물성이 결정되었다.

Hydrocarbon resins, which are defined as low molecular weight, amorphous, and thermoplastic polymers, are widely used as tackifier for various types of adhesives, as processing aids in rubber compounds, and as modifiers for plastics polymers such as isotactic polypropylene. Typically, hydrocarbon resins are non-polar, and thus highly compatible with non-polar rubbers and polymer. However, they are poorly compatible with polar system, such as acrylic copolymer, polyurethanes, and polyamides. Moreover, recently the raw materials of hydrocarbon resin from naphtha cracking had been decreased because of light feed cracking such as gas cracking. To overcome this problem, in this study, novel hydrocarbon resins were designed to have a highly polar chemical structure which material is sustainable. And, it was successfully synthesized by Diels-Alder reaction of dicyclopentadiene monomer and sorbic acid from blueberry as renewable resources. Acrylic resins were formulated with various tackifiers solution including sorbic acid grafted hydrogenated dicyclopentadiene hydrocarbon resins in acrylic adhesive and rolling ball tack, loop tack, 180° peel adhesion strength, and shear adhesion strength were measured. The properties depend on the softening point and polar content of tackifiers.

**Keywords:** Hydrocarbon resin (HCR), Tackifier, Sorbic acid, Acrylic resin, Dicyclopentadiene (DCPD), Rolling ball tack, loop tack, 180° Peel adhesion strength, Shear adhesion strength

### 1. Introduction

Hydrocarbon resin (HCR), which are defined as low

molecular weight, amorphous, and thermoplastic polymers, are widely used as tackifier for various types of adhesives, as processing aids in rubber compounds, and as modifiers for paint and ink products, and for plastics polymers such as isotactic polypropylene. Commonly,

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pressure sensitive adhesive tapes contain a HCR and base polymer, such as natural rubber, synthetic rubber or block copolymer. The hydrocarbon resins develop the mobility of base polymer at taping process as a diluent, as well as improve the peel strength at peeling process. Many researchers[1-9] and we[10,11] investigated the mechanism of tackiness development by the addition of HCRs. Pressure-sensitive adhesives (PSA) are used for many different applications in the form of tapes, labels, decals, medical products, and others. There are several types of PSA such as natural rubber-based PSA, block-copolymer-based (SIS, SBS, etc.) PSA, and acrylic PSA. The former two types of PSA are blends of rubbery polymers and hydrocarbon resin, and it used to be believed that no tackifier is needed in acrylic PSA because one can easily produce polymers of various properties by combining different kinds of co-monomers. However, recently, HCR, which polar group was modified, are often added to the formulations of acrylic PSA to modify the practical performances. Therefore, it can be said that most of the PSA actually used are blends of long-chain molecules and bulky oligomeric materials. The most important practical performance of PSA are adhesion (peel adhesion strength), tack (probe tack, ball tack, and loop tack), and holding power (shear adhesion strength), and because they are all closely related to deformation and failure of the materials, the measured values are dependent not only on temperature but also on rate of deformation[12]. There are three types of HCR which are C5, C9, and hydrogenated dicyclopentadiene (DCPD). Especially a hydrogenated DCPD HCR, typically manufactured by DCPD monomer from naphtha cracking in the course of the thermal polymerization and hydrogenation processes, is used in hot melt adhesive, hot melt PSA, solvent based PSA, and so on. However, a hydrogenated DCPD HCR consists of carbon and hydrogen molecules, so it is impossible to apply to acrylic polymer because of poor compatibility with acrylic polymers containing ester groups as a polar polymer. More recently, instead of petroleum-based raw materials due to environmental problem, the eco-friendly renewable resources being used to meet green technology are a major issue for industry. As mentioned above, in HCR industry, the eco-friendly HCR has lately become a subject of special interest. In a different way, the raw materials of HCR from naphtha cracking had been decreased because of light feed cracking such as gas

cracking, so new raw materials to make HCR is essential. On the other hands, to diversify the application of HCR, high polar HCR having good compatibility with polar polymer such as acrylic resin is necessary to be developed. To be satisfied with above factors, the renewable resources as the substitute of raw materials of HCR is worth being considered. There are many kinds of renewable resources in the world. In this paper, the sorbic acid from blueberry was tested.

## 2. Experimental

**Materials.** Sorbic Acid, DCPD, toluene, and xylene were from Sigma Aldrich (99% Purity). Tackifiers were a terpene-phenol tackifier (Tamanol-803 from Arakawa chemical), hydrogenated dicyclopentadiene tackifier (SU-130 from Kolon Industries Inc. in Korea). Acrylic resin (BA1250W) and acrylic hardener (45S) are from Burim chemical in Korea. Pd/Al Catalyst (HD-101, 0.5% Pd) is from BASF.

**Sorbic acid grafted hydrogenated DCPD HCR preparation.** Sorbic acid and xylene were mixed with DCPD monomer in 1 L autoclave as the blend ratios of 0/50/50, 5/50/45, 10/50/40, 15/50/35, and 20/50/30 (Sorbic acid/Xylene/DCPD). The mixture was polymerized for 1 h at 275°C. After finishing polymerization step, put the metal catalyst 5 parts to the mixture and it was hydrogenated for 1.5 h at 80 kgf/cm<sup>2</sup>, 230°C. Finally, the product was got from the evaporation step to get rid of non-reacted monomer for 10 min. at 5 torr, 240°C.

**Blend Preparation and Coating.** 40 wt% solutions of tackifier in toluene were prepared. The solution of tackifier with acrylic resin of the blend ratios of 100/0 and 90/10 (Acrylic resin/Tackifier) by weight were prepared. 1 wt% of Acrylic hardener was imparted to the solutions of tackifier with acrylic resin. After coating the solution on PET film, it was dried at 130°C for 2 min.

**Molecular Weight.** The molecular weights and molecular weight distributions of tackifiers were measured using a Waters GPC (Column : HR-1, HR-2, HR-3, HR-4). The solvent used was tetrahydrofuran (THF). A refractive index detector was used. Polystyrenes with different molecular weight values were used as the calibration material.

**FT-IR(Fourier Transform Infrared Spectroscopy).** The FT-IR spectrum was recorded on a Perkinelmer Spectrum 100 FT-IR Spectrophotometer in transmittance mode, with

4 cm<sup>-1</sup> resolution and with 40 accumulations. The frequency range of 400~600 cm<sup>-1</sup> was covered. The KBr (150 mg) pellets were prepared on a quartz mortar with about 4.5 mg (ca.3%) of sample. The sample was then transferred to a metal container and pressed at 8 ton for a min to afford pellets of width 0.55 mm.

**Gardner Color.** The 50 wt% solution of HCR in toluene was checked as its Gardner # by Colorimeter. The lower value of Gardner # means the better color property.

**Softening Point.** The softening point of tackifier was checked by Automatic Softening Point Tester (Meitech Com.) with speed of 5°C/min.

**Oxygen Content.** The oxygen content in the tackifiers were measured by an Elemental Analyzer (FlashEA™ 1112, Thermo Fisher Scientific Inc., USA).

**Tack.** The ChemInstruments TT-100 rolling ball tack tester, meets the standards set by the Pressure Sensitive Tape Council's Method No.6[13] (PSTC-6) and the ASTM (ASTM D3121), was used for testing the tack of pressure sensitive adhesives. *The PSA was coated on the PET film with 25 μm in width. It was dried for 2 min at 130°C oven.*

**Loop Tack.** The PSA was coated on the PET film with 25 μm in width. It was dried for 2 min at 130°C oven. The Chem Instruments LT-1000 loop tack tester, the steps involved in the test was described below.

Step a : Initial flat strip

Step b : Form the loop from the tape. The specified length of tape should be bent back until around 10 mm or so of the ends are in contact.

Step c : Clamp the loop in the movable test machine grips. The formed loop should be connected to a load measuring device with sufficient range and sensitivity. The loop should be aligned such that the edges of the tape will be at a right angle to the edge of the base plate.

Step d : Lower the loop. The loop should be lowered, pushing down onto the base surface, until the tape makes contact over the required area.

Step e : Pull the loop off the surface. Once the loop has contacted the required area of the base plate, the direction of the test machine should be reversed.

The loop tack was measured both initial value after drying and aging value after aging for 3 days at 70°C oven.

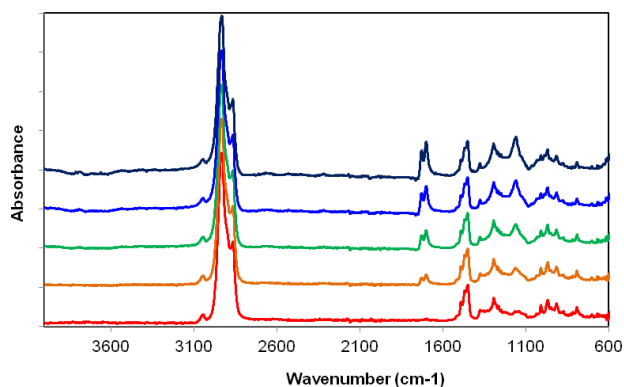
**180° Peel adhesion.** 180° Peel adhesion test method

(PSTC-1, Peel adhesion for single coated tapes at 180° Angle) was used to measure the adhesion strength of PSA. The PSA was coated on the PET film with 25 μm in width. The PSA on the PET film was cut into strip with 25 mm in width and was placed on a stainless steel panel (SUS304, ChemInstruments Com. in USA) used as the substrate. This assembly was served as a test specimen and the prepared specimen was pressed using a 2 kg iron roller to develop good contact between the adhesive and the stainless steel panel. The iron roller was moved backward and forward once, which was defined as one press cycle. Test specimens were subjected by two press cycles. The prepared specimens were left to hold for 20~40 min. before being subjected to peel adhesion tests. The 180° peel adhesion was measured at a peel rate of 300 mm/min. at room temperature by Universal Test Machine Model H5KT (Hounsfield).

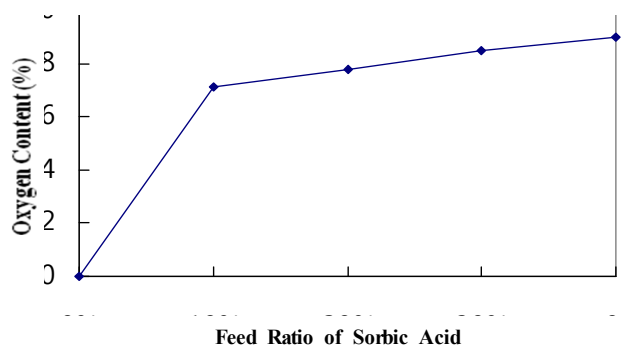
**Shear adhesion strength (holding power).** Shear adhesion (holding power) test, PSTC-7 or ASTM D3654[14] was used to measure the cohesive strength of PSA. The PSA was coated on the PET film with 25 μm in width. The PSA on the PET film was cut into strip with 25 mm in width and was placed on a stainless steel panel (SUS304, Chem Instruments Com. in USA) used as the substrate. This assembly was served as a test specimen and the prepared specimen was pressed by using a 2 kg iron roller to develop good contact between the adhesive and the stainless steel panel. The iron roller was moved backward and forward once, which was defined as one press cycle. Test specimens were subjected by two press cycles. The prepared specimens were left to hold for 20~40 min. before being subjected to cohesion tests. Finally, the prepared specimens were placed in the shear adhesion rack with extending tape hanging downward and 1 kg weight was secured to the free end with an appropriate hook. The time for total separation to occur was measured for shear adhesion strength at 80°C.

### 3. Results and Discussion

In HCR industry, the eco-friendly hydrocarbon resin has lately become a subject of special interest. In a different way, the raw materials of HCR from naphtha cracking had been decreased because of light feed cracking such as gas cracking, so new raw materials to make HCR is essential. On the other hands, to diversify the



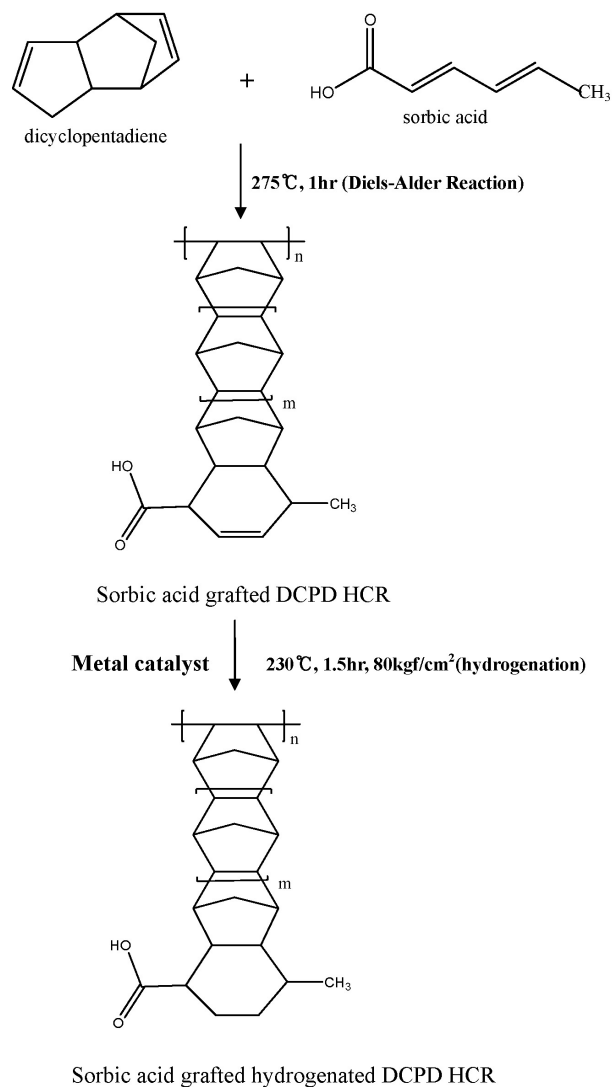
**Figure 1.** FT-IR Chart of (a) Sorbic acid content : 0%, (b) Sorbic acid content : 10%, (c) Sorbic acid content : 20%, (d) Sorbic acid content : 30%, (e) Sorbic acid content : 40%.



**Figure 2.** The polarity of hydrogenated sorbic acid grafted DCPD HCR by element analyzer.

application of HCR high polar HCR having good compatibility with polar polymer such as acrylic resin is necessary to be developed. To be satisfied with above factors, the renewable resources as the substitute of raw materials of HCR is worth being considered. Sorbic acid as renewable resource was successfully grafted to DCPD monomer, which is a commonly used for manufacturing a HCR, to make new HCR for decreasing carbon dioxide during processing. It is known that the conjugation monomer like sorbic acid reacts with DCPD diels-alder reaction[15].

Generally, tackifier like synthetic HCR has no polar group, so it has poor compatibility with acrylic adhesive. But sorbic acid grafted hydrogenated DCPD HCR has high polar group and good compatibility with acrylic adhesive. FT-IR data of sorbic acid grafted hydrogenated DCPD HCR shows Figure 1. Its manufacturing scheme shows Scheme 1. Figure 2 Shows the polarity of sorbic acid grafted hydrogenated DCPD HCR. Its other physical properties show Table 1. Figure 1 show that the sorbic acid was surely grafted with DCPD monomer by diels-al



**Scheme 1.** Elementary manufacturing steps for sorbic acid grafted hydrogenated DCPD HCR.

der reaction because there is carbonyl peak (C=O) from sorbic acid exists at  $1730\text{ cm}^{-1}$  in FT-IR. Moreover, as the content of sorbic acid is increased, the intensity of the carbonyl peak is also increased. Scheme 1 shows the elementary manufacturing step for sorbic acid grafted hydrogenated DCPD HCR. As the content of sorbic acid was increased like Figure 2 the oxygen content of sorbic acid grafted hydrogenated DCPD HCR was increased. Table 1 shows that the softening point and molecular weight was also increased as the content of sorbic acid was increased.

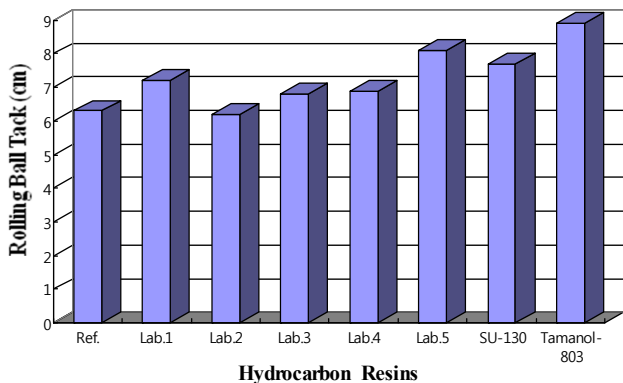
Table 2 shows the used tackifier for formulating acrylic adhesives. Figure 3 shows rolling ball tack property of acrylic resin/ tackifier solution blend according to

**Table 1.** Typical Properties of Sorbic Acid Grafted Hydrogenated DCPD HCR

Sorbic acid content (%) to DCPD	Softening Point (°C)	Molecular Weight (Mw)	Color (Gardner#, 50% Solution in Toluene)
0	122	680	1.5
10	128	860	1.8
20	132	1,050	2.0
30	140	1,200	2.2
40	142	1,420	2.3

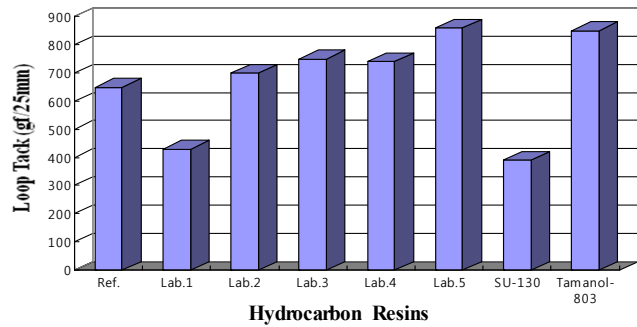
**Table 2.** Types of Used Tackifier for Formulating Acrylic Adhesive

Tackifier	Sorbic acid content (%) to DCPD	Softening Point(°C)	Remark
Lab.1	0	122	Lab. Production
Lab.2	10	128	
Lab.3	20	132	
Lab.4	30	140	
Lab.5	40	142	
SU-130	-	130	Commercial Production
Tamanol-803	-	150	Commercial Production

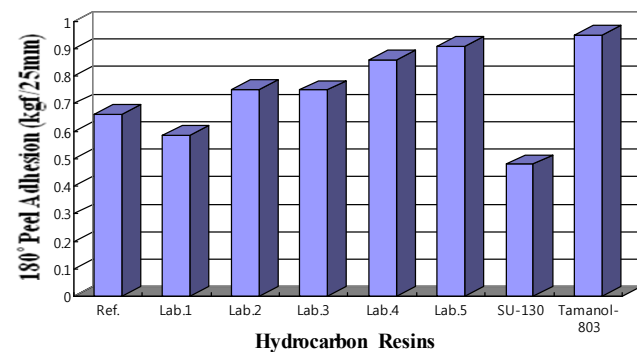


**Figure 3.** Rolling ball tack of solvent based acrylic resin/ Tackifier blends (Ref. : Acrylic resin/Tackifier = 100/0 wt%, Others : Acrylic resin/Tackifier = 90/10 wt%).

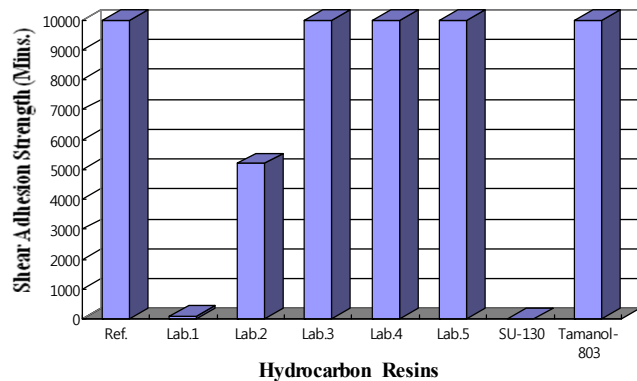
the types of tackifier. According to the result, the rolling ball tack depends on the softening point. So called, the PSAs formulating tackifier with high softening point has worse tack property than reference. Figure 4 shows loop tack property of acrylic resin/tackifier solution blend according to the types of tackifier. According to the result, the loop tack depends on the compatibility. So called,



**Figure 4.** Loop tack on SUS panel of solvent based acrylic resin/ Tackifier blends (Ref. : Acrylic resin/ Tackifier = 100/0 wt%, Others : Acrylic resin/ Tackifier = 90/10 wt%).



**Figure 5.** 180° Peel adhesion on SUS panel of solvent based acrylic resin/Tackifier blends (Ref. : Acrylic resin/ Tackifier = 100/0 wt%, Others : Acrylic resin/ Tackifier = 90/10 wt%).



**Figure 6.** Shear adhesion strength at 80°C on SUS panel of solvent based acrylic resin/ Tackifier blends (Ref. : Acrylic resin/ Tackifier = 100/0 wt%, Others : Acrylic resin/ Tackifier = 90/10 wt%).

the PSAs formulating tackifier with high polar content such as Lab.2~5 and Tamanol-803 have better loop tack property than reference. Figure 5 shows 180° peel adhesion strength on SUS substrate. According to the result, the 180° peel adhesion strength depends on the

compatibility tackifier with acrylic resin. So called, the PSAs formulating tackifier with high polar content such as Lab.2~5 and Tamanol-803 have better 180° peel adhesion strength than reference because those have good compatibility with acrylic resin. But the PSAs formulating tackifier with no polar content such as Lab.1 and SU-130 have worse 180° peel adhesion strength than reference. Figure 6 shows the shear adhesion strength on SUS substrate. According to the result, the shear adhesion strength depends on the softening point of tackifier and compatibility tackifier with acrylic resin. According to the result, the PSAs formulating tackifier with high softening point and high polar content such as Lab.2~5 and Tamanol-803 have similar shear adhesion strength with control.

#### 4. Conclusions

The sorbic acid grafted hydrogenated DCPD HCR, which applied newly a sorbic acid as renewable resource, was successfully synthesized. It has high polar content to give good compatibility with acrylic resin in adhesive industry. The PSA formulated various HCRs including sorbic acid grafted hydrogenated DCPD HCR with acrylic resin were measured rolling ball tack, loop tack, 180° peel adhesion strength, and shear adhesion strength. The higher polar content of HCR has better performance for acrylic adhesives.

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