

EVA계 핫멜트 접착제의 조성이 접착력에 미치는 영향

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Effect of Composition of EVA-based Hot-Melt Adhesives on Adhesive Strength

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요약: 접착부여수지의 종류와 함량을 달리하여 에틸렌비닐아세테이트 공중합체(Ethylene Vinyl Acetate Copolymer, EVA)를 베이스 폴리머로 하는 핫멜트 접착제를 제조하고, 그것들의 유변학적 거동과 폴리우레탄 기재에 대한 T-peel 접착력을 평가하였다. C5 지방족 석유수지, C9 방향족 석유수지, 수소가 첨가된 디사이클로펜타디엔 석유수지 그리고, 디사이클로펜타디엔/아크릴 모노머 공중합 석유수지가 각각 핫멜트 접착제의 접착부여수지로 사용되었다. 접착부여수지의 산소 함량을 분석하여 접착부여수지의 극성도를 측정하였는데, 디사이클로펜타디엔/아크릴 모노머 공중합 석유수지가 다른 접착부여수지보다 산소 함량이 높은 것을 확인하였다. 디사이클로펜타디엔/아크릴 모노머 공중합 석유수지만이 EVA와 완전한 혼화성을 보였고, 핫멜트 접착제는 모든 조성에서 균일상을 나타내었다. 핫멜트 접착제와 폴리우레탄 기재와의 T-peel 접착력은 핫멜트 접착제 자체의 저장탄성계수(G')보다는 핫멜트 접착제에 첨가된 접착부여수지의 극성도에 의해서 좌우됨이 확인되었다.

Abstract: A series of ethylene vinyl acetate (EVA) based hot melt adhesives containing different types and compositions of tackifier resins were prepared to investigate their rheological behavior and T-peel adhesion strength on polyurethane (PU) elastomeric sheets. C5 aliphatic hydrocarbon resin (C5 resin), C9 aromatic hydrocarbon resin (C9 resin), hydrogenated dicyclopentadiene resin (H₂-DCPD resin), and dicyclopentadiene and acrylic monomer copolymer resin (DCPD-acrylic resin) were used as the tackifiers for the hot melt adhesives. To determine the polarity of the tackifiers, their oxygen contents were analyzed, and the DCPD-acrylic resin was found to contain an oxygen content higher than the other tackifiers. Only the DCPD-acrylic resin showed complete miscibility with EVA and the homogeneous phase of the hot melt adhesive blends at all compositions. The T-peel adhesion strength between the hot melt adhesives and polyurethane elastomeric sheets was mainly affected by the polarity of the tackifier resins in the hot melt adhesives, rather than by the storage moduli, G', of the hot melt adhesives themselves.

Keywords: hot melt adhesives (HMA), tackifier, hydrocarbon resin, T-peel adhesion strength, oxygen content, rheological property

1. Introduction

Hot-melt adhesives (HMAs) are gaining importance in all areas of adhesive usage, because of their superior properties and environmental concerns about solvent based

adhesives[1]. HMAs are widely used for spreading over substrates in the melt state, followed by solidifying after cooling[2]. They are used for cartons, boxes, trays, aluminum foil, cans, bookbinding, disposable diapers and sanitary products[3-5]. HMAs are mixtures of three different components, namely polymers, tackifiers and waxes. The polymer contributes strength and toughness, while the

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tackifier enhances the wetting and tack properties. The waxes are included to lower the melt viscosity and reduce the cost. The antioxidant reduces the thermal degradation during processing. For the base polymers of the hot-melt adhesives, thermoplastics, such as ethylene vinyl acetate copolymer (EVA), polyolefins, polyamides, and polyesters, are often used[2]. Among these polymers, EVA is widely used as the base polymer for various types of HMA. Tackifiers are generally formulated in EVA-based HMAs. Because they have a high glass transition temperature (T_g) and low molecular weight, compared to EVA, the addition of tackifiers increases the T_g and the storage modulus at high strain rates[6], while lowering the storage modulus at low strain rates. The tackifiers also act as a diluent to lower the entanglement density, resulting in a decreased plateau modulus[7]. The relation between viscoelasticity and adhesive properties of EVA/tackifier resin blends has been investigated by research groups[8-15]. The hydrocarbon resins, which are used as tackifiers in HMAs, can be classified according to whether they contain primarily aromatic, aliphatic, or dicyclopentadiene (DCPD) monomers. These are also referred to as C9, C5, and C10, respectively, corresponding to the average number of carbon atoms per monomer molecule. Recently, new types of hydrocarbon resin were developed and commercialized, for example, DCPD-acrylate copolymer hydrocarbon resin.

In general, EVA-based HMAs are widely used in various substrates and show good adhesion strength. However, they often have limited adhesion strength on polar substrates such as polyurethane (PU) elastomers. Typically, the properties (molecular weight, T_g and chemical structure) of the tackifier affect the miscibility and performance of the HMA[16-18]. Especially, the polarity of the tackifiers can cause the HMA to have different adhesion strengths on various adherends. In this article, four different resins (C5 resin, C9 resin, hydrogenated DCPD resin and DCPD-acrylate copolymer resin) are used as the tackifier for HMAs. The polarity of the tackifier, which can be inferred from its oxygen content, was determined. The rheological properties of the blends of EVA and tackifier were measured and interpreted. Then, the adhesion properties (T-Peel adhesion strength on polyurethane sheet) of the blends were measured[19-21].

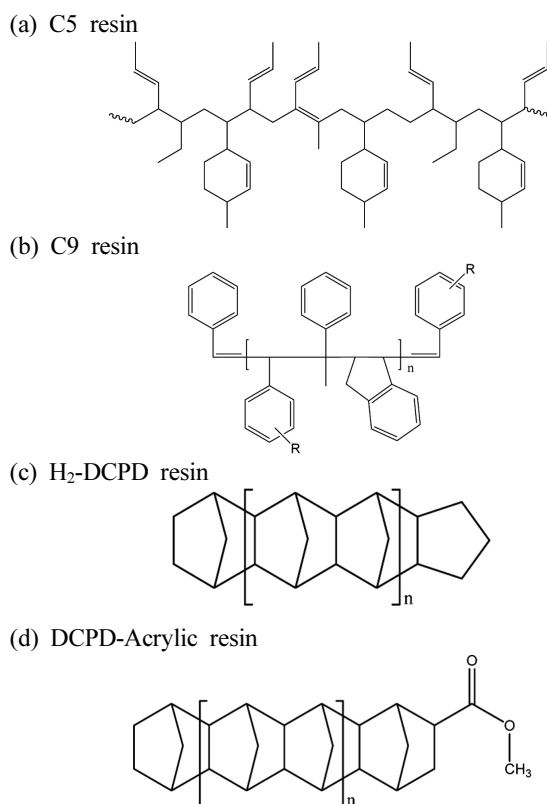


Figure 1. Chemical structure of tackifiers : (a) C5 resin, (b) C9 resin, (c) H₂-DCPD resin, and (d) DCPD-Acrylic resin.

2. Experimental

2.1. Materials

Four tackifiers were used; the first is an aliphatic hydrocarbon resin (C5 resin ; Hikorez A-1100, KOLON Ind., Inc.), the second is an aromatic hydrocarbon resin (C9 resin; Hikotack P-90, KOLON Ind., Inc.), the third is a hydrogenated dicyclopentadiene (DCPD) resin (H₂-DCPD resin; SU-100, KOLON Ind., Inc.) and the last is a hydrogenated acrylic monomer modified DCPD resin (DCPD-acrylic resin ; PX-95, KOLON Ind., Inc.). The chemical structures of the tackifiers, suggested by KOLON Ind., are illustrated in Figure 1. Ethylene vinyl acetate copolymer (EVA ; VA910, Honam Petrochemical Corp.) was used as the base polymer for the HMA. Some characteristics of the EVA copolymer, such as the melt index, vinyl acetate content and the molecular weight, are shown in Table 1. To reduce the thermal degradation, 0.5 parts by weight of antioxidant (AO ; Songnox 1010, Songwon Industrial Co., Ltd.) was added in the preparation of the HMA.

Table 1. EVA used in this study

Properties	EVA	Test method
Melt index, g/10 min	400	ASTM 1238
Vinyl Acetate Content, wt%	28	HPC method
Tg, °C	-28.6	DSC
Softening point, °C	65	ASTM E 28
Mn	21,041	GPC
Molecular Weight	73,748	
Mz	172,084	
MWD	3.50	

EVA : Ethylene vinyl acetate copolymer (HPC, VA910)

Table 2. Tackifiers used in this study

Properties	C5	C9	C10	CA	Test Method
Softening Point, °C	100	99	101	100	ASTM E 28
Tg, °C	48	50	52	51	DSC
Color, Ga.#	4	4	0.2	1	ASTM D 1544
Oxygen Content, wt%	0.2	0.3	0.2	9.1	E.A
Mn	920	820	410	560	GPC
Molecular Weight	1,610	1,190	570	880	
Mz	3,430	1,800	970	1,200	
MWD	1.75	1.45	1.39	1.57	

C5 : C5 hydrocarbon resin (KOLON, HIKOREZ[®] A-1100)C9 : C9 hydrocarbon resin (KOLON, HIKOTACK[®] P-90)C10 : H₂-DCPD resin (KOLON, SUKOREZ[®] SU-100)

CA : DCPD-acrylic resin (KOLON, PX-95)

2.2. Characterization of Tackifiers

The glass transition temperature (T_g) of the tackifiers was measured by differential scanning calorimetry (DSC 2910, TA Instruments, USA) with a heating rate of 10°C/min. The molecular weight of the tackifiers was measured by Gel Permeation Chromatography (GPC, Waters, USA). The oxygen content in the tackifiers was measured by an Elemental Analyzer (FlashEA[™] 1112, Thermo Fisher Scientific Inc. USA). The detailed characteristics are listed in Table 2.

2.3. Preparation of HMAs

EVA was mixed with the tackifiers in a 300 g internal mixer at 50 rpm with a machine temperature of 180°C. First, the tackifier and antioxidant were added. The quantity of antioxidant, Songnox 1010, was 0.5 parts per hundred of the adhesive compounds. When the tackifier became masticated and formed a homogeneous melt, the EVA was slowly added until completion. The mixing time was about 20 min. EVA and the tackifier were blended

Table 3. Formulations of samples (parts by weight)

Sample	Components					
	C5	C9	C10	CA	EVA	Antioxidant
C5M-3	30				70	0.5
C5M-5	50				50	0.5
C5M-7	70				30	0.5
C9M-3		30			70	0.5
C9M-5		50			50	0.5
C9M-7		70			30	0.5
C10M-3			30		70	0.5
C10M-5			50		50	0.5
C10M-7			70		30	0.5
CAM-3				30	70	0.5
CAM-5				50	50	0.5
CAM-7				70	30	0.5

at various ratios of 70 : 30, 50 : 50, and 30 : 70. The detailed sample designations and formulations are listed in Table 3.

2.4. Physical Characterization of HMAs

The glass transition temperatures (T_g) was measured using differential scanning calorimetry (DSC 2910, TA Instruments, USA). The samples were first cooled to -80°C, and then heated to 120°C at 10°C/min. They were kept at this temperature for 2 min. Then, the samples were cooled to -80°C and scanned to 120°C at 10°C/min. The results of the second run were used in this study. The rheological properties of the hot melt adhesives were measured on a TA instruments AR 2000. The specimens with a thickness of 2 mm and diameter of 8 mm were prepared and measured at a shear rate of 1 Hz. The testing temperatures were in the range of -50 to 120°C with a heating rate of 7°C/min.

2.5. T-peel adhesion strength of HMAs

To measure the T-peel adhesion strength the HMA films were prepared by coating the hot melt adhesives on release paper with a thickness of 50 µm. PU sheets were used as the adherends. The dimensions of the PU sheets are shown in Figure 2. The test specimens used for the T-peel adhesion strength test were prepared according to the conditions presented in Figure 2. The adhesion temperature and pressure were 150°C and 20 kgf/cm², respectively. These specimens were conditioned at 20°C (65% relative humidity) for 1 week before testing to en-

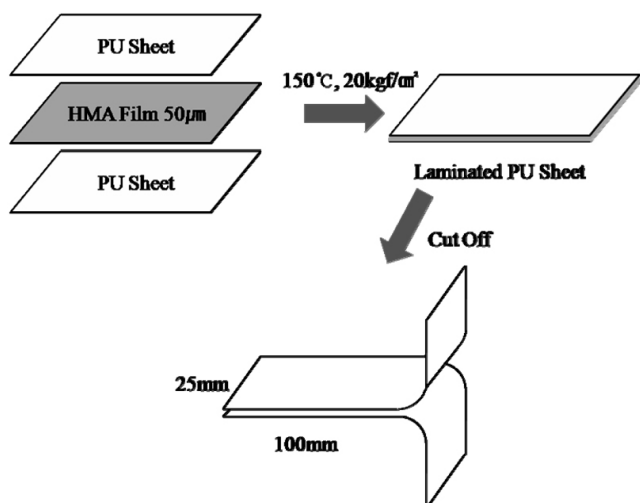


Figure 2. Test specimen for T-peel adhesion strength test.

sure that the adhesives were completely in the equilibrium state. The measurement of the T-peel adhesion strength was conducted with an Instron device with a cross-head speed of 200 mm/min at a temperature of 20°C. The test results are the average of five measurements made under the same conditions.

3. Results and Discussion

3.1. Characteristics of Tackifiers

The properties of the tackifiers are listed in Table 2. All of the tackifiers are amorphous with no melting points. All of the materials have one glass transition temperature at around 50°C. The molecular weights of the tackifiers are small, compared to those of elastomers or other polymeric materials. In contrast with the other tackifiers, PX-95, which is a copolymer resin with DCPD and acrylic monomer, has a higher oxygen content (9.2 wt%), suggesting that it has a higher polarity level than the others. This is caused by the modification of the acrylic monomer.

3.2. Thermal Properties of HMAs

In general, T_g measured by DSC is widely used for determining the miscibility of polymer blends. The thermograms in Figure 3 show T_g and the melting temperature (T_m) of HMAs. When C5 resin or C9 resin was used as the tackifier, the T_g of HMA only slightly increased with increasing the resin content. However, the T_g of HMA using H₂-DCPD resin or DCPD-acrylic resin, increased significantly with the resin content. Therefore, H₂-DCPD or DCPD-acrylic resin could be considered to have

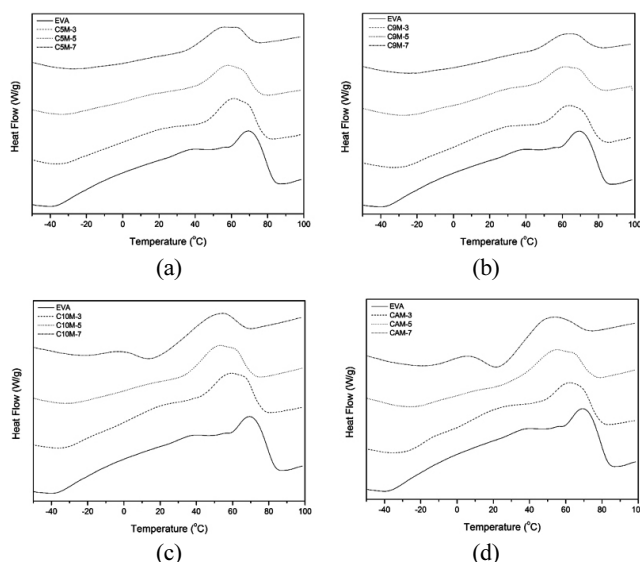


Figure 3. DSC thermograms of HMA containing different tackifier : (a) C5 resin, (b) C9 resin, (c) H₂-DCPD resin, and (d) DCPD-acrylic resin.

Table 4. Melting temperature of HMAs

Tackifier	Tackifier concentration (wt%)	T_m (°C)
C5	0	70.4
	30	62.1
	50	59.4
	70	55.9
C9	0	70.4
	30	65.9
	50	61.8
	70	62.7
C10	0	70.4
	30	59.9
	50	53.2
	70	53.1
CA	0	70.4
	30	64.7
	50	55.5
	70	51.6

better miscibility with EVA than C5 resin or C9 resin. In Table 4 the T_m of HMA using H₂-DCPD resin or DCPD-acrylic resin was lower than the other HMAs. It could be interpreted that HMAs with H₂-DCPD resin or DCPD-acrylic resin show similar level of miscibility with EVA and the melt flow characteristics in the elevated temperatures.

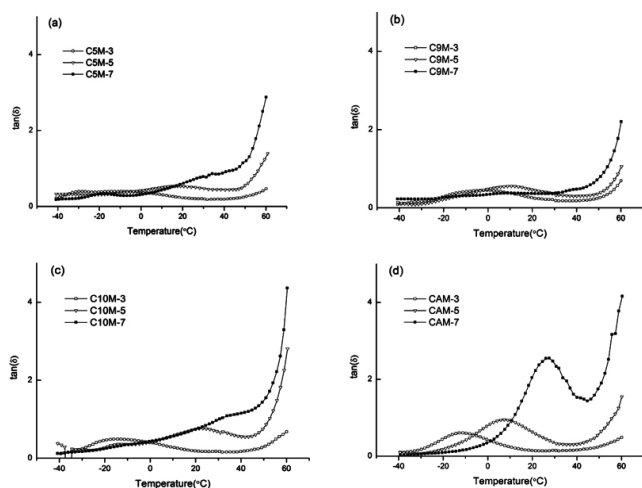


Figure 4. $\tan \delta$ of HMA containing different tackifier : (a) C5 resin, (b) C9 resin, (c) H₂-DCPD resin, and (d) DCPD-acrylic resin.

3.2. Rheological Properties of HMAs

The $\tan \delta$ versus temperature plots for the HMAs made using the various tackifiers are shown in Figure 4. It is quite clear that the C5 resin and EVA are incompatible at all compositions. There are two overlapping peaks at C5 resin contents of 30, 50, and 70 wt%, suggesting the existence of two phases. A similar trend is seen for the C9 resin and EVA, where there is no clear peak which can be discerned as the glass transition temperature. The H₂-DCPD resin and EVA are not completely compatible when the concentration is above 50 wt% H₂-DCPD resin, but they are compatible at a resin content of 30 wt%. There is a single peak at an H₂-DCPD resin content of 30 wt%, however, it is difficult to distinguish whether there is only one peak or two overlapping peaks at H₂-DCPD resin contents of 50 and 70 wt%.

At all of the compositions, the blends of DCPD-acrylic resin and EVA show a single peak, which means that they are homogeneous and consist of a single phase. For a single phase resin, the Fox equation can be used to predict its glass transition temperature. By means of this equation and the $\tan \delta$ peak temperature from Figure 4, the T_g of the DCPD-acrylic resin is calculated to be 47 and 56°C, based on the results from the blends with 30 and 50 wt% of resin, respectively. The average value, 51.5°C, is close to the T_g found by DSC.

The storage moduli (G') of the various HMAs are plotted in Figure 5. Except at low temperatures the G' values of HMAs with the 70 wt% tackifier are higher than those with the 50 wt% tackifier, when the tackifier

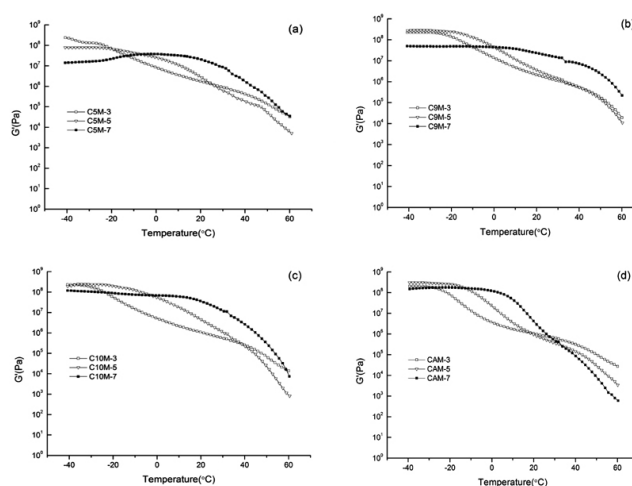


Figure 5. Storage modulus of HMA containing different tackifier : (a) C5 resin, (b) C9 resin, (c) H₂-DCPD resin, and (d) DCPD-acrylic resin.

is C5 resin, C9 resin or H₂-DCPD resin. Also, when the temperature is higher than the T_g of the tackifiers, the G' values of the HMAs with DCPD-acrylic resin are less than those with C5 resin, C9 resin or H₂-DCPD resin. If the tackifier is miscible in EVA, it would act as a plasticizer, diminishing the degree of entanglement of EVA, thereby decreasing the storage modulus at the higher temperature corresponding to the T_g of the tackifier. This behavior was previously reported and an explanation for it was proposed by Kraus and Hanshimoto[22]. Thus, three resins, C5 resin, C9 resin and H₂-DCPD resin, are not completely miscible with EVA in the resin-rich phase. However, the G' values of the blends with DCPD-acrylic resin gradually decreased at temperatures above the T_g of the DCPD-acrylic resin, as seen in Figure 5(d). These findings suggest that only DCPD-acrylic resin is completely compatible with EVA at all compositions.

3.3. Adhesion strength of HMA

The T-peel adhesion strength of the HMAs on the PU sheets are shown in Figure 6. The strength of the C5 resin and EVA blends are close to zero at all compositions, which means that there is no interfacial adhesion strength between the HMAs with C5 resin and the PU sheet. The blends with C9 resin show significant strength (higher than 1 kgf/25 mm) at a resin content of 50 wt%. However, in the other compositions, the adhesion strength is insignificant. The blends with H₂-DCPD resin have a lower adhesion strength than those with C9 resin. Although the storage moduli, G' , of the HMAs with DCPD-acrylic res-

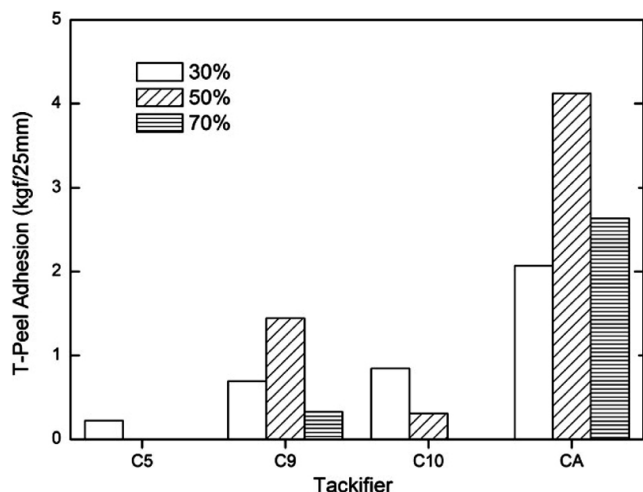


Figure 6. T-peel adhesion strength of HMA on PU substrate (cross-head speed = 200 mm/min).

in are lower than those of the other HMAs at the temperature of the T-peel adhesion strength test (Figure 5), they show outstanding adhesion strength on the PU sheets, compared to the other HMAs. This finding suggests that when a high polarity tackifier, as determined by its oxygen content, is mixed with EVA, the resultant HMAs show better wettability and superior adhesion strength on polar adherends such as PU sheets.

4. Conclusion

A series of model HMAs based on EVA resin and the tackifier were prepared and their properties were characterized. The polarity of a tackifier was determined by the analysis of its oxygen content and DCPD-acrylic resin had a very high content of oxygen of 9.2 wt%, in contrast to the common hydrocarbon tackifier resins having an oxygen content of almost zero. When C5 resin or C9 resin was blended with EVA, they showed a heterogeneous phase at all compositions. H₂-DCPD resin and EVA were not completely compatible when the concentration of the resin was above 50 wt%, but they were compatible at a resin content of 30 wt% and showed a homogeneous phase. HMA blends with DCPD-acrylic resin showed complete compatibility with EVA and a homogeneous phase at all compositions. The T-peel adhesion strength between HMAs blended with DCPD-acrylic resin and PU sheets were much superior to those of the other HMAs. Normally, the T-peel adhesion strength of the tackified EVA can be controlled by tuning the viscoelastic response, i.e., the higher the G' value is,

the higher the T-peel strength is. However, in this study, the adhesion strength between the tackified EVAs and PU sheets was mainly controlled by adjusting the polarity of the tackified EVA, which was dependent on the polarity of the tackifier.

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