

New Branched Oxo Alcohol Based Acrylates for Pressure Sensitive Adhesive Applications

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Introduction

Pressure sensitive adhesive (PSA) designates a type of polymeric material that when dried, is aggressively and permanently tacky at room temperature. A PSA will firmly adhere to a variety of similar or dissimilar surfaces upon mere contact with no more than finger pressure.

Acrylic PSAs can be either solventborne, waterborne emulsion or the more recent 100% solids UV curable hot melt. Pressure sensitive adhesive compositions are useful for a wide variety of applications such as labels, tapes, decals, decorative and protective sheets, medical and other specialty areas.

Three properties critical to PSAs are tack, peel (adhesion) and shear strength (cohesion). To achieve desired performance, acrylic PSAs are produced using a combination of monomers. The monomer mixture typically includes one or more soft monomers such as butyl acrylate (BA) or 2-ethyl hexyl acrylate (2-EHA), to impart good tack and deformability, and one or more hard monomers such as methyl methacrylate, styrene or vinyl acetate, to provide the cohesive strength. Small amounts of functional monomers such as acrylic acid (AA) or methacrylic acid (MAA) and 2-hydroxyethyl acrylate, are also typically used to provide crosslinking points and improve adhesion characteristics to highly polar substrates. Adhesive properties are affected by a number of factors such as polymer compositions, molecular weight, glass transition temperature (T_g), morphology, gel content and formulations which may incorporate plasticizer, tackifiers or crosslinkers. Due to the underlying structure mechanism contributing to these properties, the attempts to improve one property (e.g. cohesion) by using hard monomer or crosslinking would typically result in the reduction in the other performance properties (e.g. adhesion) such as peel and tack.

Another critical property for PSA tape is water resistance when used in outdoor (extended moisture/water exposure) or other indoor high moisture applications. Also in certain label applications such as bottles labeled with clear film, the construction can be subjected to pasteurization conditions where the label is expected to remain clear through the process. A high degree of resistance to water whitening by the PSAs is required. Historically, solventborne PSAs are used in such demanding applications, however, market trends¹ have pushed for the adoption of emulsion based PSA in these applications. Emulsion based PSA is made in water and

stabilized by surfactants which are water sensitive. Upon drying, these hygroscopic ingredients, depending on the film formation process and compatibility with the polymer, will distribute throughout the polymer film in different ways such as residing inside the latex particles, aggregating in the interstitial areas, and/or blooming to the surface or interface of the substrate. These surfactants, along with the hydrophilic monomers such as AA or MAA of the PSA polymer composition, could result in poor water resistance, and poor water whitening if these hydrophilic species aggregate into small domains. Upon extended exposure to water or high moisture conditions, these aggregates will absorb sufficient water to form enlarged and hydrated domains which eventually manifest themselves as the so called water whitening or haziness appearance.

Over the last few decades, tremendous efforts and progress have been made in the PSA industry to provide even higher performance, better environmental compliance in traditional applications and customized properties for new applications such as electronics and opticals. Nevertheless, the limited selection of commercially available soft monomers such as butyl acrylate and 2-ethylhexyl acrylate, which are based on butanol and 2-ethylhexanol respectively, places a constraint on the best performance potentially achievable. On the other hand, although linear long chain alcohol based acrylate is known to crystallize and not be suitable for PSA application, acrylates derived from more branched alcohols such as oxo alcohols have not received sufficient attention in PSA application. Oxo alcohols are a type of alcohols derived from hydroformylation of olefins and the oxo alcohols used in current study have average branching indexes anywhere from 1 to more than 3². As a comparison, butanol and 2-ethylhexanol have 0 and 1 branches respectively. In this paper, oxo alcohol based acrylates with carbon number ranging from 8 to 13 were used as the soft monomers to prepare a series of pressure sensitive adhesives. The performance of these PSA polymers were evaluated in the following two areas of adhesion/cohesion balance and water (whitening) resistance. The relationship between oxo alcohol structure and adhesive property will also be discussed.

Experimental

Materials

Polymer Synthesis

A surfactant solution was prepared by dissolving 1.0g of anionic emulsifier A in 45g of deionized water. A monomer mixture of 31g 2-ethylhexyl acrylate (2EHA), 31g butyl acrylate (BA), 12g methyl methacrylate (MMA), 3g hydroxyethyl acrylate (HEA), 3g acrylic acid (AA) and 0.08g 1-dodecanethiol was added to the surfactant solution prepared above and the mixture was agitated for 15mins to make a monomer pre-emulsion. Separately 0.3g of ammonium persulfate (APS) was dissolved into 10g of deionized water to prepare the initiator solution. For the polymerization, to a 500ml four-neck flask equipped with a thermometer, mechanical stirrer and condenser was added with 25g deionized water, 0.1g APS and 0.2g anionic emulsifier A. With stirring, the flask is heated to 82°C and 10 wt.% of the pre-emulsion of monomer (12.6g) was added to the flask within 15 min and the seed polymerization was allowed to proceed for 15mins. The remaining monomer pre-emulsion and initiator solution were fed simultaneously into the reactor within 3.5h and 4h, respectively. Upon finishing the initiator addition, the polymerization was held for another 1h at 85°C. After the hold process, the obtained latex was

cooled to room temperature, filtered, adjusted the pH value to 7.5~8 by ammonia solution, and bottled.

Similarly, emulsion polymers based on oxo alcohol derived acrylates were also prepared by replacing the same amount of 2EHA with the respective oxo alcohol derived acrylates.

Test Methods

Glass transition temperature (T_g): T_g of the PSA polymers are measured by Netzsch DSC 204F differential scanning calorimeter (Germany).

Gel fraction: About 2g of dried latex film is wrapped by one piece of filter-paper which was then extracted continuously with tetrahydrofuran (THF) under reflux for 24h at 70°C to remove the soluble components. After extraction, the gel left in the filter-paper was dried and weighed. Gel fraction is calculated as the following equation:

$$\text{Gel fraction (wt\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\%$$

where W_0 , W_1 , and W_2 are the weight of filter-paper, the initial polymer with filter-paper, and polymer after extraction with filter-paper, respectively.

Tack property: The rolling ball tack property is measured per GB/T 4582-2002 (China).

Shear resistance: The shear property is measured per GB/T 4581-2014 (China).

180° peel strength: The peel strength is measured per GB/T 2792-2014 (China).

Results and Discussion

Basic properties of homopolymers

Although the properties of BA and 2EHA homopolymers are well known in literature, there is no comprehensive report of the properties of the homopolymers of branched oxo alcohol derived acrylates. A thorough understanding of the fundamental properties of these homopolymers will help to maximize the benefits of these oxo alcohol based acrylates and formulate a copolymer PSA product with excellent properties.

Table 1: Physical parameters of oxo alcohol derived acrylates

	Average Alcohol carbon #	Branching index	T_g , °C	M_e	Literature M_e
BA	4	0	-47	31K	17K-26K
2EHA	8	1	-68	59K	35K-130K
Oxo C8 acrylate	8	1.6	-57	77K	-
Oxo C9s acrylate	9	1.8	-55	-	-
Oxo C10 acrylate	10	2	-58	100K	-
Oxo C11 acrylate	11	2.2	-	-	-
Oxo C13 acrylate	13	3.1	-59	-	-

Glass transition temperature of the oxo alcohol based acrylates and some typical soft monomers measured in our lab are listed in Table 1. Compared with a Tg of -47°C for BA and -68°C for 2EHA, oxo 8 based acrylate have a Tg of -57°C, 11°C higher than the 2EHA isomer. With the oxo alcohols carbon number increasing from 8 to 13, Tg does not decrease as would be expected with the more linear alcohol based acrylate, but instead stabilize at around -57°C to -58°C, roughly half way between BA and 2EHA. Also listed in Table 1 is the entanglement molecular weight (M_e) calculated from the zero shear modulus at frequency corresponding to the lowest $\tan\delta$ of the homopolymer DMTA master curve rheology. As a comparison, the literature reported M_e from BA and 2EHA are also listed here^{3, 4}. The lab generated M_e of BA shows somewhat higher M_e than the literature reported data and the M_e of 2EHA is within the range of the literature reports, which has significant discrepancies. It is believed these discrepancies were caused by polydispersity effect where low molecular weight species originating from different polymerization conditions act as plasticizer that increases M_e ⁵. Nevertheless, for the homopolymers made in-house under identical conditions, the more branched oxo alcohol derived acrylate shows directionally higher entanglement molecular weight than 2EHA and BA. Both unique attributes of the oxo alcohol derived acrylates are related to the higher branching structure which could alter both the monomer polymerization behavior and polymer physical properties. The next sections of this paper will discuss how these unique properties could be exploited to enhance the performance of the PSA copolymers.

Adhesion Properties of copolymer PSA

Prototype formula based on Table 2 were used to prepare emulsion copolymer PSAs which comprise of 38.75% 2EHA (control) or oxo alcohol derived acrylates and the remaining monomers are BA, MMA, HEA and AA. Figure 1 is the glass transition temperatures of the acrylic PSA copolymers. Notably Tg of the PSA polymers in Figure 1 based on oxo alcohol derived acrylates are a few degrees higher than the PSA based on 2EHA due to the branched structure of the oxo alcohol which increases the rigidity of the polymer, probably due to the increased barrier to rotation around the backbone bonds⁶.

Table 2 Emulsion polymerization formula

Reagents		Total Amount (gram)
Deionized Water (H ₂ O)		80
Anionic emulsifier A		1.2
Monomer Mixture	MMA	12
	BA	31
	AA	3
	Oxo alcohol derived acrylate or 2EHA	31
	2-HEA	3
	Chain Transfer Agent(CTA)	0.08
Ammonium Persulfate(APS)		0.4

Solid content: 50%

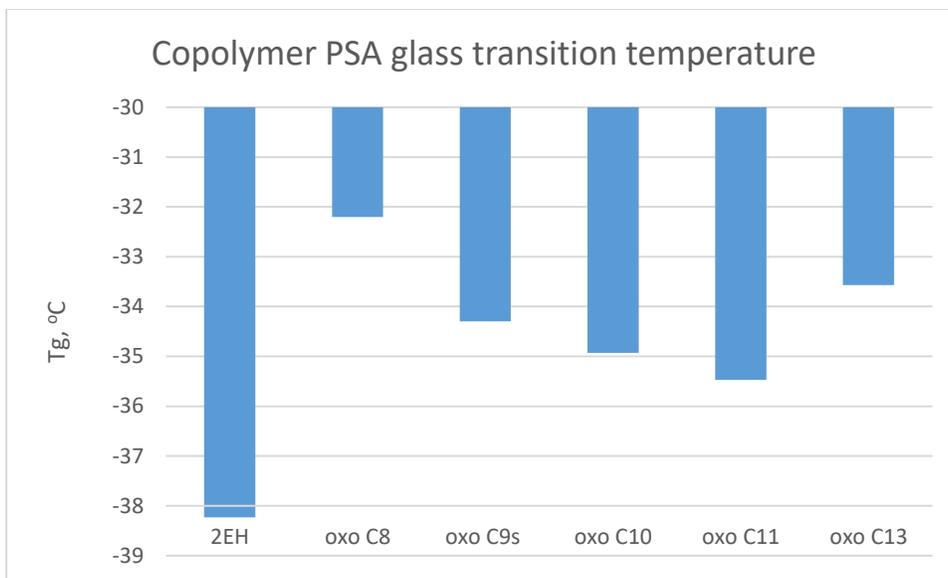


Figure 1: Glass transition temperature of the copolymer PSAs

The three key properties, shear, peel and tack of these PSA copolymers were evaluated. For PSAs, cohesion and adhesion have a delicate balance and the approaches to improve one property often result in the decrease of the other property⁷. With 2EHA or BA as the soft monomers, typical approaches to increase shear strength such as using multi-functional crosslinkers or hard monomers result in a sacrifice of peel strength. However, this type of compromise could be resolved to a great extent with oxo alcohol derived acrylates. Figure 2 shows the adhesion properties of these copolymer PSAs. As the data shows, PSAs based on oxo alcohol derived acrylates achieved remarkably higher shear strength than the PSA based on 2EHA. High cohesive/shear strength are typically related to high molecular weight, internal or external crosslinking. Indeed, Soxhlet extraction of the PSA polymers with THF revealed that PSAs incorporating oxo alcohol derived acrylates consistently have higher gel content than the 2EHA based PSA (Figure 3) which suggests a more tightly cross-linked network than 2EHA/BA based control polymer. No major difference in shear strength was observed among the various oxo alcohol acrylates derived PSAs. On the other hand, with much increased shear strength, PSAs based on oxo alcohol derived acrylates maintained comparable high peel strength as 2EHA control which suggest a much better peel shear strength balance. The reason could be due to a higher entanglement molecular weight and more hydrophobic nature of the monomer which has increased mobility and could wet the substrate better, therefore achieving a more intimate interface contact beneficial for adhesion, while the higher gel fraction helps with cohesion of the PSA polymer. The PSA rolling ball tack property is measured per GB/T 4582-2002 (China) in which a strip of PSA film is placed onto a slope with an angle of 30°, and steel balls of different size are released from the top of the slope. The tack is represented by the largest size of the balls which after rolling down the slope could stop within the PSA test strip film range. With this test, oxo C8 and C9 derived acrylate based PSAs show comparable tack properties as 2EHA based PSA while the higher alkyl oxo alcohol derived PSAs show slightly lower tackiness.

Enhanced adhesion/cohesion balance offered by oxo alcohol based acrylates could broaden the formulation window in PSA product developments. For example, it might be possible to formulate a high peel and tack PSA by adding tackifiers while maintaining an adequate shear strength.

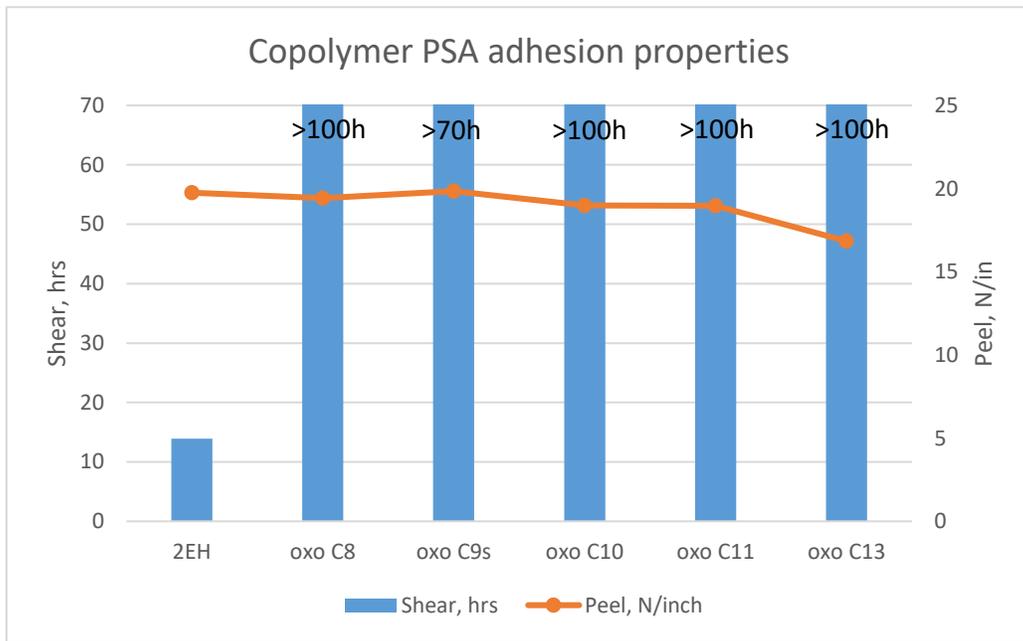


Figure 2: Peel and shear properties of copolymer PSAs

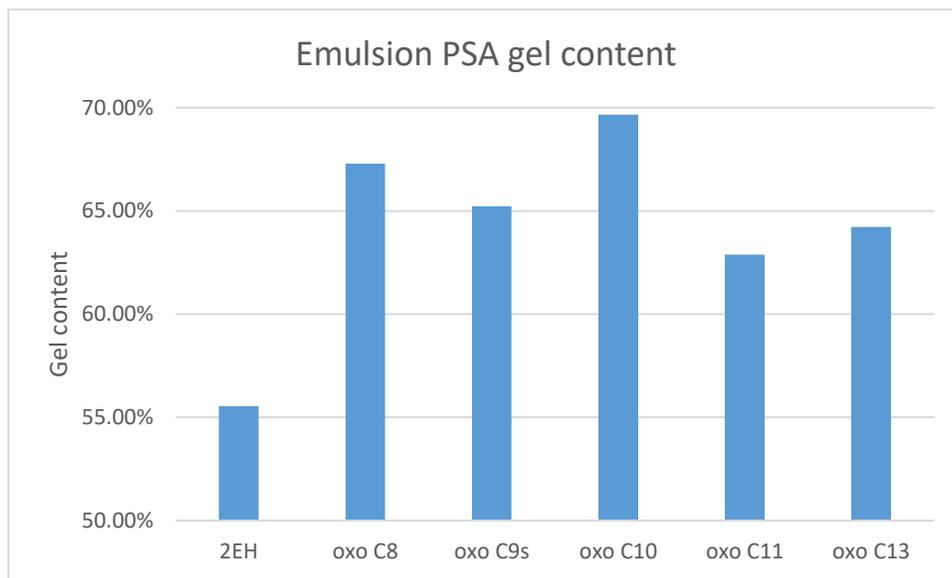


Figure 3: Gel contents of copolymer PSAs

Water (Whitening) Resistance

In addition to the adhesion performance evaluation, the emulsion PSA made above are also evaluated for water resistance by water absorption, water contact angle and water whitening resistance. Figure 4 is the water absorption study of the PSA polymer based on the formula of Table 1 and also the equivalent percentage replacement with oxo alcohol based acrylates. The polymer made from 2EHA as a reference has a water absorption rate of 25% after 24h water soak. The oxo C8 based PSA has a higher water absorption rate of 30% which indicated a more hydrophilic nature of the bulk of the polymer. It is not a surprising result if considering the more branched structure of oxo C8 alcohol compared with 2EH. Indeed, studies⁸ have compared the properties of linear and branched alkyl ethoxylate surfactants and showed that the CMC of the branched ethoxylate surfactant is about 3 to 4 times higher than the linear counterparts. It was concluded that branching of the hydrophobe could be in effect equivalent to chain length reduction, and therefore result in a more hydrophilic nature. Moving from oxo C8 up to oxo C11, the water absorption rate decreased significantly from 30% for oxo C8 to about 17% for oxo C11. PSA derived from oxo C13 alcohol surprisingly had a very high water absorption rate of 88%. The exact reason is not clear, presumably is due to the difficulty to polymerize this much more hydrophobic monomer and results in unreacted monomers and poorly coalesced film.

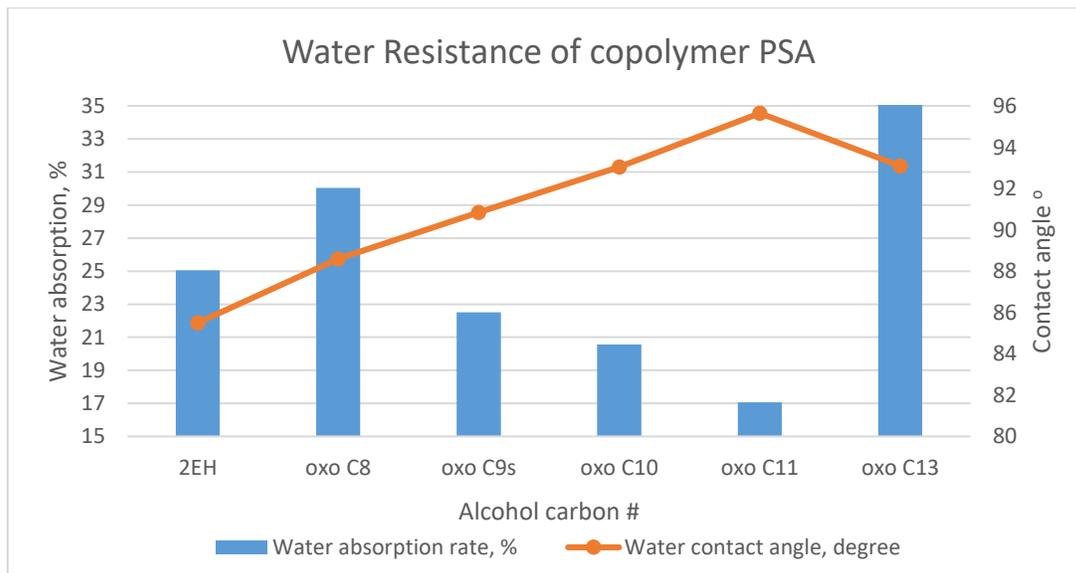


Figure 4: Water resistance of copolymer PSAs

Also shown in Figure 4 is the water contact angle comparisons of these PSA polymer films. oxo C8 alcohol based PSA has a higher water contact angle than 2EHA based PSA which suggests a more hydrophobic nature. This appears to be in contradiction to the water absorption results above. However, it must be pointed out that the water absorption results are relevant to the bulk property of the polymer, while the contact angle is about the surface nature of the polymer film. With the more branched structure, oxo C8 moiety of the polymer could function as an umbrella and create a more hydrophobic surface than the more linear 2EH based PSA and therefore result in a higher contact angle. Similar observations have been reported for neodecanoic acid vinyl ester based emulsion polymers⁹. It was also reported that branched alcohol based ethoxylates have lower minimum surface tension than same carbon number linear alcohol based ethoxylates at their respective CMC, which also suggested a more hydrophobic interface between the water/air interface¹⁰. For PSAs based on oxo alcohol derived acrylates, with the carbon number

increasing from 8 to 11, water contact angle increased from 89° to 96° while the contact angle decreased slightly for oxo C13 to 93° which is likely due to the same reason discussed above.

Figure 5 shows the water whitening resistance test results of the PSA films soaked in water at room temperature for 2h and 24h. At 2h, the 2EHA based PSA already started to show cloudiness, while oxo C10 and C11 are still transparent and there is no sign of water whitening. Oxo C8 and C9 based PSA show slightly better whitening than 2EHA at 2h water soaking. Even with a longer soaking time of 24h, while oxo C10 and C11 starts to show the sign of water whitening, the whitening is much more severe with 2EHA based PSA as evidenced from the pictures. It must be understood that this particular formula is a model formula and not optimized for the water/water whitening resistance application. Although there are reports of achieving water whitening resistance using relative large amount of hydrophilic monomers, these PSA polymers typically suffer from poor water resistance. With the study results in this paper, it is now possible to achieve both superior water whitening and water resistance properties simultaneously through a combination of using oxo alcohol derived acrylates and formulation optimization.

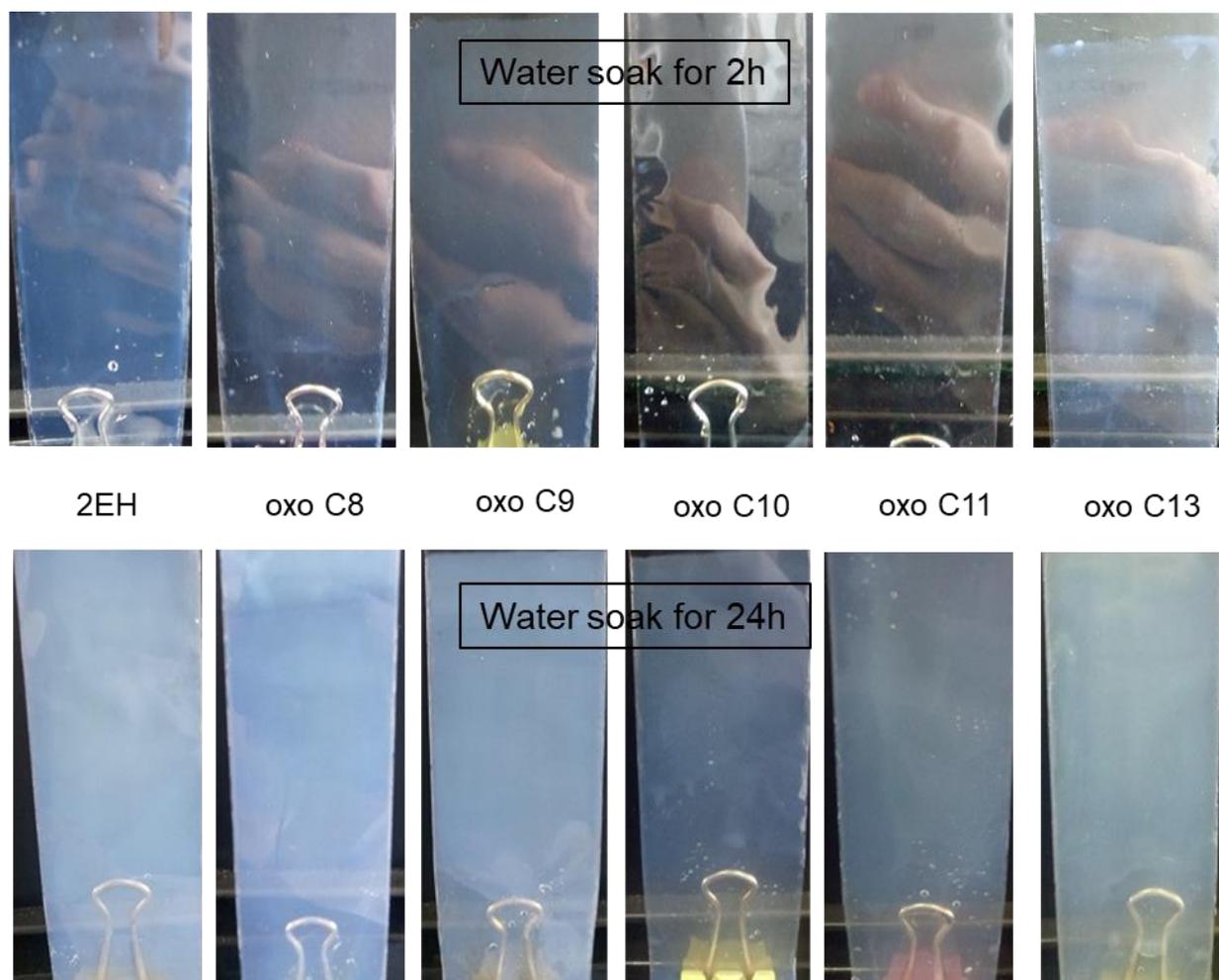


Figure 5 Water whitening resistance of copolymer PSAs

Overall, oxo alcohol derived acrylates possess distinctive properties compared to the more linear 2EHA, such as branchiness and glass transition temperature. In the model formula study, PSA polymer based on oxo alcohol derived acrylate with 8 or more carbons on the alcohol moiety demonstrated a plurality of positive effects such as better adhesion/cohesion balance and improved water/(water whitening) resistance. These monomers along with the unique properties discussed above, certainly could provide a powerful toolbox for the adhesive formulators to achieve their stringent performance requirements. Further extensive study of oxo alcohol derived acrylate's effect on other key properties of PSA are being explored and will be reported in the near future.

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