

Adapted from the paper presented at PSTC May 16-18, 2007 Orlando, FL

DEVELOPMENT OF OLEFIN BLOCK COPOLYMERS FOR PRESSURE SENSITIVE ADHESIVES

C. Li Pi Shan, S. Yalvac, C. Diehl, G. Marchand, C. Rickey, T. Karjala
The Dow Chemical Co.
Specialty Plastics and Elastomers R&D
Freeport, TX

T. Carvagno, P.M. Dunckley, L. Germinario
Eastman Chemical Company
Kingsport, TN

Introduction

Over the past 10 years, polyolefin-based elastomers have found opportunities in hot melt adhesives and non-woven construction adhesives. For hot melt adhesives, low viscosity metallocene copolymers offer superior stability, better processability, low color and odor, better adhesion, and better economics in terms of mileage and lower maintenance cost over the incumbent polymers such as ethylene vinyl acetate (EVA). However, one deficiency has been the balance of softness and high temperature resistance for adhesion over the broad window of temperatures required for pressure sensitive adhesive applications.

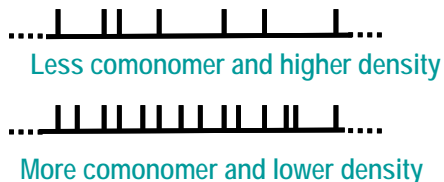
We are introducing block copolymers based solely on ethylene and α -olefin monomers made using INSITETM catalyst technology. Olefin block copolymers (OBC) produced by "chain shuttling technology" have polymer chains with alternating blocks of semi-crystalline "hard" and elastomeric "soft" segments [1,2]. These blocky olefin copolymers conform to the unusual concept of a thermoplastic block copolymer by having characteristic high melting temperatures and low glass transition temperatures but are based on ethylene and alpha olefin alone (i.e., propylene, butene, hexene, octene). Structurally, these OBC's have crystalline blocks with lower comonomer content to serve as physical crosslinks to connect elastomeric blocks with higher comonomer content [2-4]. One key difference between OBC and traditional styrenic block copolymers (SBC) synthesized via living anionic polymerization is that SBC's are typically synthesized with a diblock or triblock polymer architecture whereas, due to the nature of the "chain shuttling technology", OBC's are synthesized with a random multi-block architecture that follows a statistical distribution of block lengths.

Figure 1 compares the architecture of a random ethylene- α -olefin copolymer and an olefin block copolymer. Generally, the crystallinity or density of a random copolymer is constrained by its level of comonomer and molecular weight. The random polyolefin copolymers typically used in these applications are low in crystallinity (0.87-0.88 g/cc density) and have low melting temperatures (less than 90°C). Dow's new OBC's have achieved independent control of the composition of the hard and soft blocks which results in highly differentiated material properties that break the traditional relationship of flexibility and heat resistance.

Ethylene- α -olefin: Random Vs Block Copolymer Structures

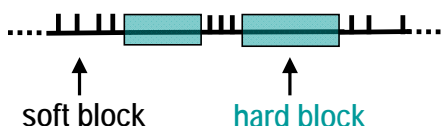
TMTrademark of The Dow Chemical Co.

Random Copolymers



- For ethylene- α -olefin random copolymers, adding more comonomer (C3, C4, C6, C8) lowers the polymer density and crystallinity & increases flexibility.
- However the melt temperature, crystallization temperature and heat resistance also drop as density is lowered.

Olefin Block Copolymers



- New catalyst technology to produce ethylene-based copolymers with alternating hard and soft blocks with different crystallinities.
- The soft blocks deliver flexibility and low temperature properties and the hard blocks deliver high temperature resistance.
- Therefore, flexibility similar to random copolymers is achieved with improved heat resistance and elasticity.

Figure 1 - Microstructure of Random and Olefin Block Copolymers

SBC's are typically polymerized using living anionic polymerization conditions which provide nearly monodispersed midblock and end block lengths and produce a polymer with a narrow molecular weight distribution (typically $M_w/M_n \approx 1.0-1.5$). In contrast, OBC's have polydisperse hard and soft segment lengths and broader molecular weight distributions ($M_w/M_n \approx 2$). Similar to other polyolefins polymerized with post-metallocene catalysts, OBC's have excellent melt processability and thermal stability (due to the absence of unsaturated groups).

In this paper, we introduce the use of OBC's for pressure sensitive adhesive applications. OBC's compatibility with tackifier and oil were investigated to provide some basic guidelines and strategies for developing starting point formulations for application development.

Experimental

Materials

The following developmental grade OBC's were used in this evaluation, as shown in Table 1. Initial screening indicated that OBC polymers with low crystallinity and higher MI were suitable to meet the formulation requirements for typical coating applications.

Table 1 - Typical properties of OBC polymers.

Designation	Density (g/cc)	Melt Index (12.16 kg @ 190°C)	Approx. Wt% Hard Segment	Melting Point (°C)	Room Temperature G' (Pa)	Glass Transition (°C)
OBC A	0.866	21	15	117	4.6×10^6	-48
OBC B	0.877	15	30	120	1.1×10^7	-50

Adhesive Compounding and Characterization

The formulations were prepared and mixed in a *Brabender* Plasti-Corder Model DR-2072 using roller-type mixing blades at 150°C and 80-100 rpm. The polymer was pre-processed in a full bowl for 10 minutes prior to being used in a formulation. The pre-processed polymer was added to the bowl, and tackifying resin was added in portions. After complete resin addition, the blend was mixed for five minutes; mixing time was extended to 30 minutes if a styrene block copolymer was used in the formulation. Oil was added dropwise with mixing, and the completed formulation was mixed an additional 15 minutes.

Adhesive ring and ball softening point (RBSP) was tested using a Herzog ring and ball tester.

Dynamic viscoelastic properties were determined by a dynamic rheological spectrometer ARES-RDA3 (TA Instruments) in a parallel plate mode using 8-mm-diameter plates with a 1.6-1.8 mm gap. Temperature was scanned at 6°C/minute at a constant frequency of 10 rads/sec and an auto-strain range of 0.5% to 5%. The glass transition temperature (T_g) was taken as the maximum of the tan delta spectrum.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments Q1000 purged with helium using a heating and cooling rate of 20°C/min.

Atomic Force Microscopy images of tapes were collected using tapping mode on a VEECO, Dimension 3000 AFM.

Tackifier Compatibility Screening

Tackifier resins with different degrees of aliphatic and aromatic nature were tested for compatibility with OBC A. All resins were hydrocarbon-based except Mix-1, which was rosin-based. The resins were combined with OBC A in a 1:1 ratio and mixed in a Brabender at 150°C for 15 minutes. The blends were tested for their glass transition temperatures (T_g) by Differential Scanning Calorimetry and tested for their cloud point temperature.

Table 1 - Tackifiers that were tested for compatibility with OBC A

Aliphatic- Aromatic Nature	Resin*	RBSP (°C)	Mz (g/mol)
Aliphatic	<i>Regalite</i> R1090	88	1100
Aliphatic	<i>Eastotac</i> H-100L	100	2300
Aliphatic	<i>Regalrez</i> 1094	94	1350
Mixed	<i>Foral</i> 105E	100	1020
Mixed	<i>Piccotac</i> 9095	95	4250
Aliphatic	<i>Regalite</i> R1100	100	1500
Aliphatic	<i>Piccotac</i> 1095	95	3500
Mixed	<i>Piccotac</i> 8095	95	5500
Aliphatic	<i>Regalrez</i> 1126	124	2050
Mixed	<i>Regalite</i> S5100	97	1800
Aromatic	<i>Kristalex</i> 3085	85	1900

* Trademark of Eastman Chemical Company

Oil Compatibility Screening

A selection of mineral and naphthenic oils were formulated with OBC A and *Eastotac* H-100L at polymer/tackifier/oil ratio of 100/110/10 phr. The tested oils are shown below in Table 2. The formulations were coated as tapes and tested.

Table 2 - Oils of various compositions were tested for compatibility with OBC A

Oil Name*	Oil Type	Composition
<i>Kaydol</i> (Crompton-Witco)	White mineral oil	60.5% paraffinic
<i>Calsol</i> 5550 (Calumet)	Napthenic oil	
<i>Hydrobrite</i> 550 PO (Sonneborn)	White mineral oil	67.5% paraffinic
<i>Hyprene</i> P100N (Ergon-West Virginia)	Hydrotreated Paraffinic	Paraffinic
<i>ParaLux</i> 6001 (Chevron-Phillips)	Paraffinic	70 % paraffinic
<i>Hyprene</i> 60 (Ergon-West Virginia)	Severely Hydrotreated Light Napthenic	

*Trademarks of listed company.

Sample Coating

The adhesive formulations were coated onto corona treated polyester film to a coating weight of $20 \pm 2 \text{ g/m}^2$ using an in-house laboratory hot melt knife coater at 120-140°C. The tapes were faced with Chemsultants RP-12 silicone release liner, cut into one-inch wide strips, and stored at 21°C and 50% relative for one day before testing.

Tape Testing

Loop tack on stainless steel was tested on an Instron Model 4201 at 12 inch/min test rate following PSTC-16. Values are reported in ounces per square inch. Shear adhesion failure temperature (SAFT) to stainless steel was tested following PSTC-107 using a 1000g load on a one square inch sample. Initial temperature was 30 °C followed by a 0.5 °C/min ramp.

Results and Discussion

Properties of Olefin Block Copolymers

Based on an initial screening of the properties of OBC's, OBC A provided the most flexibility in terms of modulus and viscosity in PSA formulations.

Figure 2 and Table 3 compare the tensile stress-strain curves of OBC A and OBC B. These OBC's differ only by their weight % of hard crystalline segments present (15 versus 30 wt %); increasing the weight % hard segments increases the overall crystallinity of the polymer and increases its modulus. As a result, OBC A had a lower modulus and higher elongation to break than OBC B.

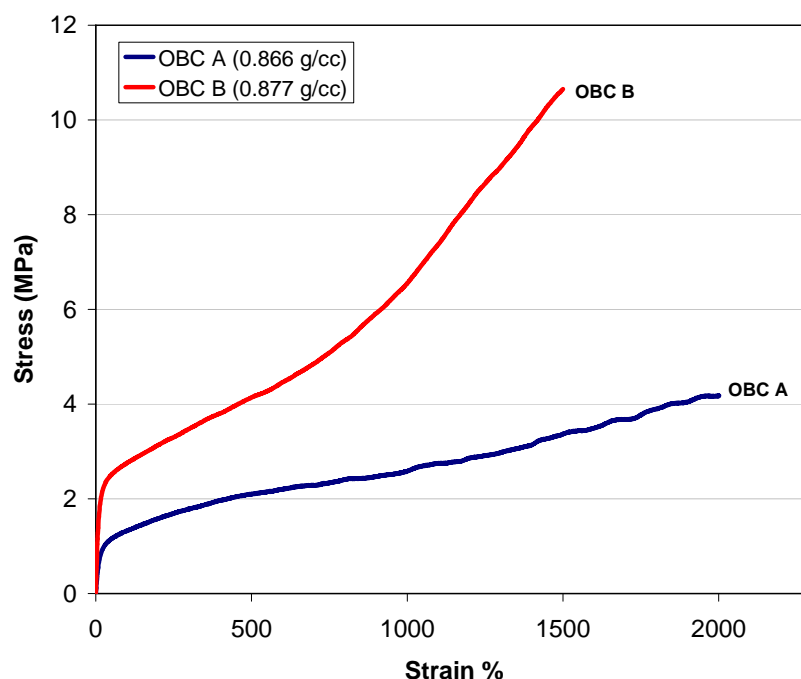


Figure 2 – Tensile Stress-Strain Behavior of OBC's

Table 3 - Tensile Properties of OBC polymers.

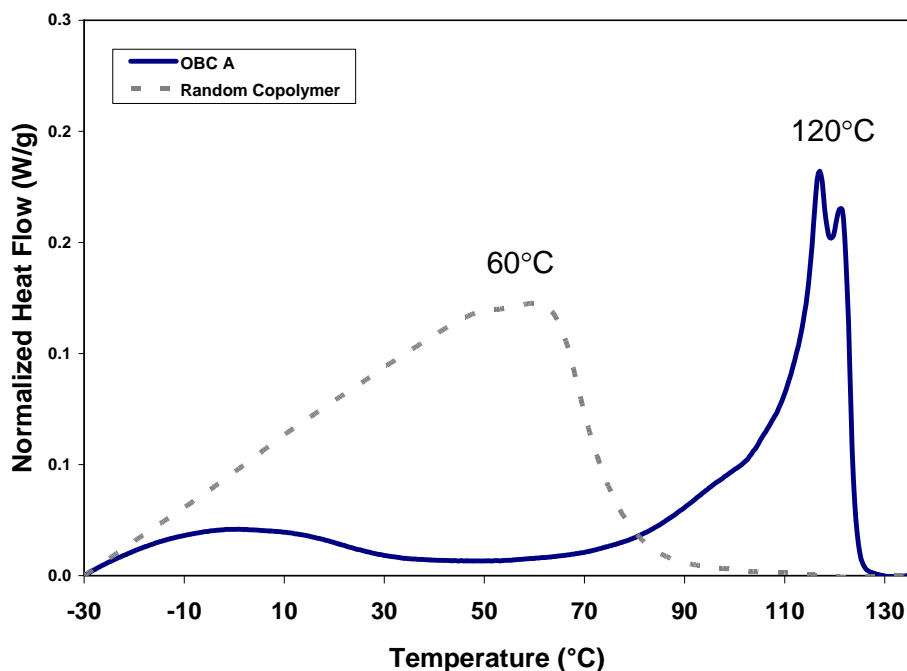
Designation	Density (g/cc)	Melt Index (12.16 kg @ 190°C)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
OBC A	0.866	15	1.3	4.0	2000
OBC B	0.877	15	3.0	11.1	1500

*Tensile measurements carried out with ASTM D638

Figure 3 compares the DSC melting profiles of OBC A and a poly(ethylene-co-octene) random copolymer (0.87 g/cc, 5MI). As shown the OBC has a significantly higher melting temperature than the random copolymer for a similar density and overall crystallinity. In comparison to SBC's, it should be noted that the high melting point of the OBC arises from the semi-crystalline hard segments that form spherulitic domains and not from glassy domains that have a high T_g.

Figure 4 compares the dynamic mechanical behavior of OBC A to a poly(ethylene-co-octene) random copolymer (0.87 g/cc, 5MI) and typical SEBS and SIS block copolymers. As shown, the G' of the OBC remains relatively high and extends past 100°C until the melting point of the polymer is reached at ~ 120°C; in comparison, the G' of the random copolymer drops precipitously after its melting point around 60°C. The plateau modulus for OBC's is more consistent over a wide temperature range than random olefin copolymers and maintains this modulus to higher temperatures than traditional SBC's.

The tan delta shows that the glass transition temperature (T_g) of the amorphous soft segments in OBC's (-48°C) are similar to that of SIS and SEBS. Having a T_g in this range allows OBC's to be used in similar formulations as SBC PSA's.

**Figure 3 – DSC Melting Profile of OBC A versus Random Copolymer**

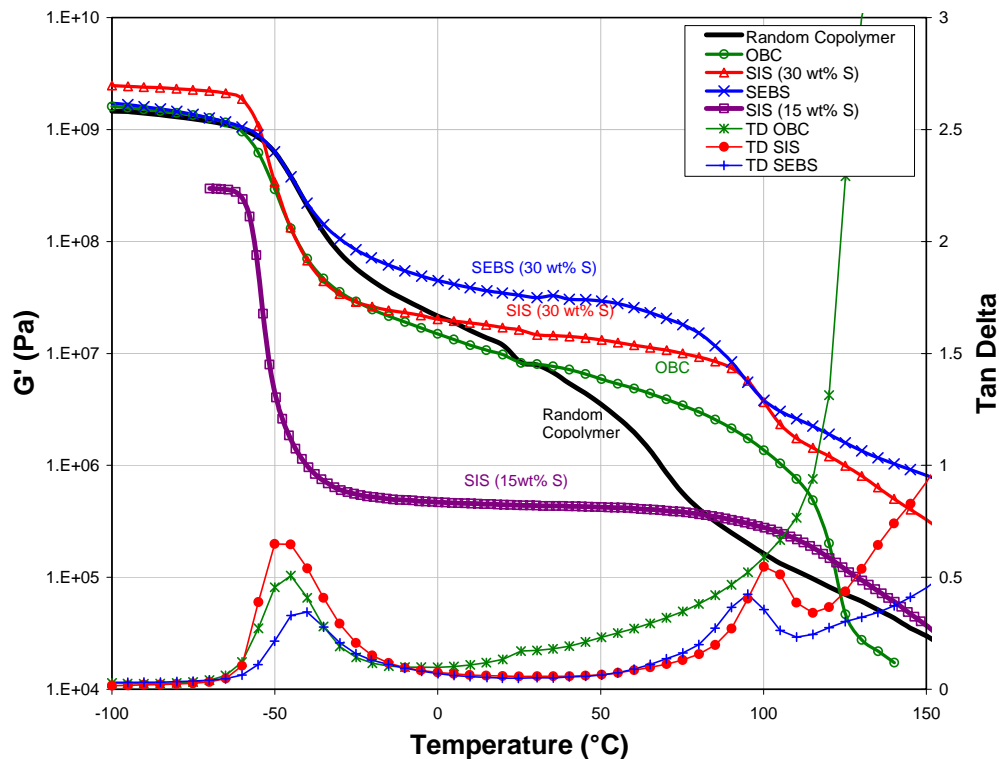


Figure 4 – Dynamic Mechanical Behavior of OBC, SBC, & Random Copolymer

To illustrate the PSA formulation capability of OBC's, Figures 5 and 6 compare the viscoelastic properties of neat OBC's and formulated OBC's to other polymers. As shown in Figure 5, neat OBC's have a similar T_g as SIS and SEBS and have room temperature G' similar to that of SEBS; notably, this particular OBC (OBC A, with 15 wt% hard segments) has a higher room temperature G' than a comparable SIS (at 15 wt% styrene). As a result of the OBC's high room temperature G' (i.e., stiffness), in order to reach the PSA window [5-7], a greater amount of tackifier resin and oil must be used.

The right hand side of Figure 5 shows some example formulations with a fully hydrogenated aliphatic tackifier resin and oil to demonstrate that OBC's can be tackified into the PSA window and are suitable for certain tape and label applications. Figure 6 compares the dynamic mechanical behavior of the formulated OBC and an SIS-based label adhesive. As shown, this formulated OBC has a T_g of -1°C and a room temperature G' of $\approx 8.5 \times 10^4$ Pa, which is in a useful temperature range for PSA. The behavior of G' for the formulated OBC is similar up to 100°C to that of the SIS-based adhesive.

Based on the PSA formulation strategy to reach a room temperature G' below that of the Dahlquist criterion [5], OBC A was the best available polymer for this study. More detail on the formulation strategy will be discussed below as OBC's have specific requirements for tackifier and oil types.

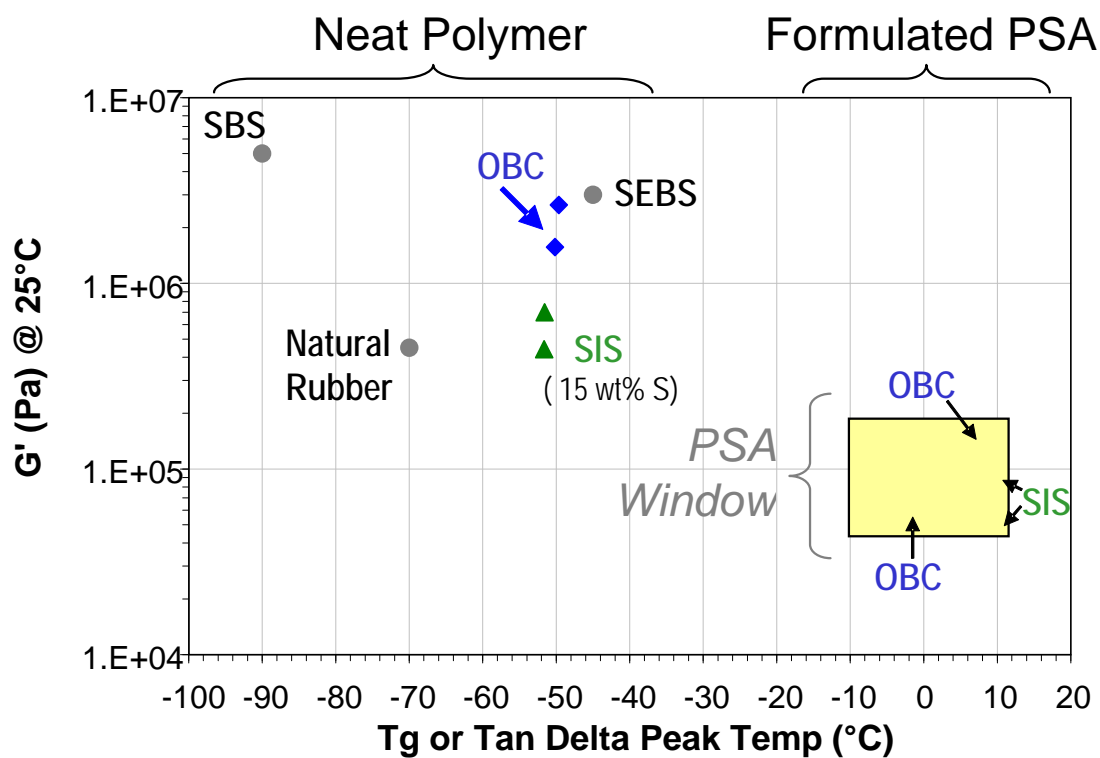


Figure 5 – PSA Viscoelastic Window for OBC's

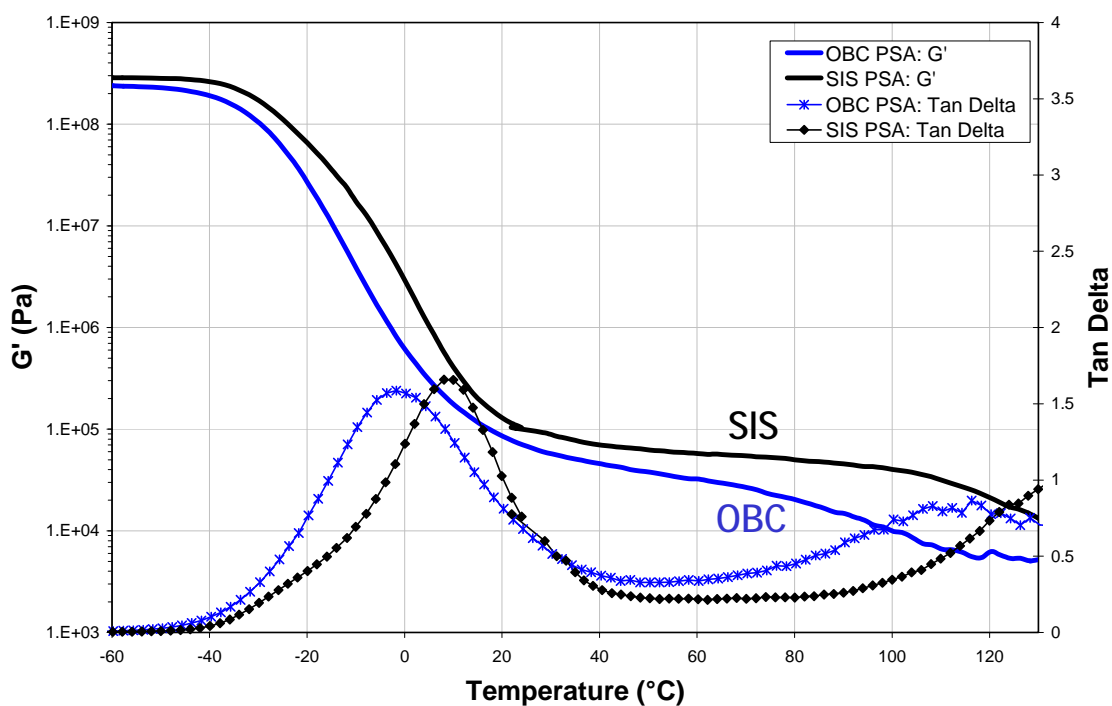


Figure 6 – Dynamic Mechanical Behavior of a Formulated OBC and SIS

Tackifier Compatibility Screening

Tackifying resins raise the T_g of a compatible polymer, and a relatively simple method to estimate the compatibility of two polymers is to measure by DSC the T_g of the mixture. The Fox equation [8] predicts the T_g of a compatible system as:

$$1/T_g = W_a/T_{ga} + W_b/T_{gb}$$

where T_{ga} and T_{gb} are the glass transition temperatures of polymers "a" and "b" in degrees Kelvin, and where W_a and W_b are the weight fraction of polymers "a" and "b". When the polymer and tackifier resin are not fully compatible, the measured T_g of the blend is lower than predicted and/or more than one T_g is detected by DSC.

The measured and calculated T_g for 1:1 blends of OBC A and various commercial tackifier resins are shown in Figure 7. None of the blends achieved the predicted T_g , and the deviation from the predicted T_g increased as the polar or aromatic nature of the tackifier resin increased. This suggests that although OBC's are most compatible with completely aliphatic tackifiers, OBC A was most compatible with aliphatic tackifier resins with molecular weights below 2500 g/mol. Further work is underway to better understand the compatibility relationship of the OBC and tackifier.

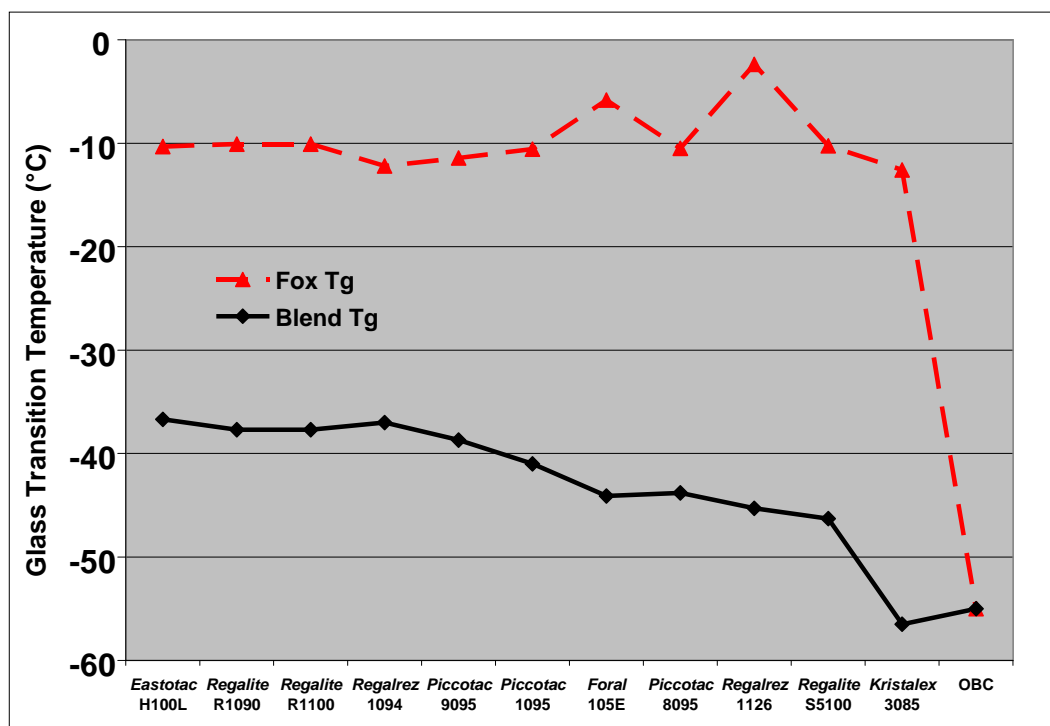


Figure 7 - Effect on T_g of blending OBC:tackifier resin at 1:1 ratio.

This trend in compatibility was also seen when measuring the full cloud point temperature of the 1:1 OBC:tackifier resin blends. A lower cloud point temperature indicates better compatibility of the blended materials. Aliphatic tackifier resins with molecular weights below 2500 g/mol gave blends that were clear when hot and cold, with a cloud point temperature below 100 °C. Aliphatic tackifier resins of moderate molecular weight formed OBC blends that were clear above 125°C (clear hot)

but reached full cloud by 100°C (opaque cold). OBC blends with tackifier resins with substantial aromatic character or high in molecular weight were opaque until at least 200 °C.

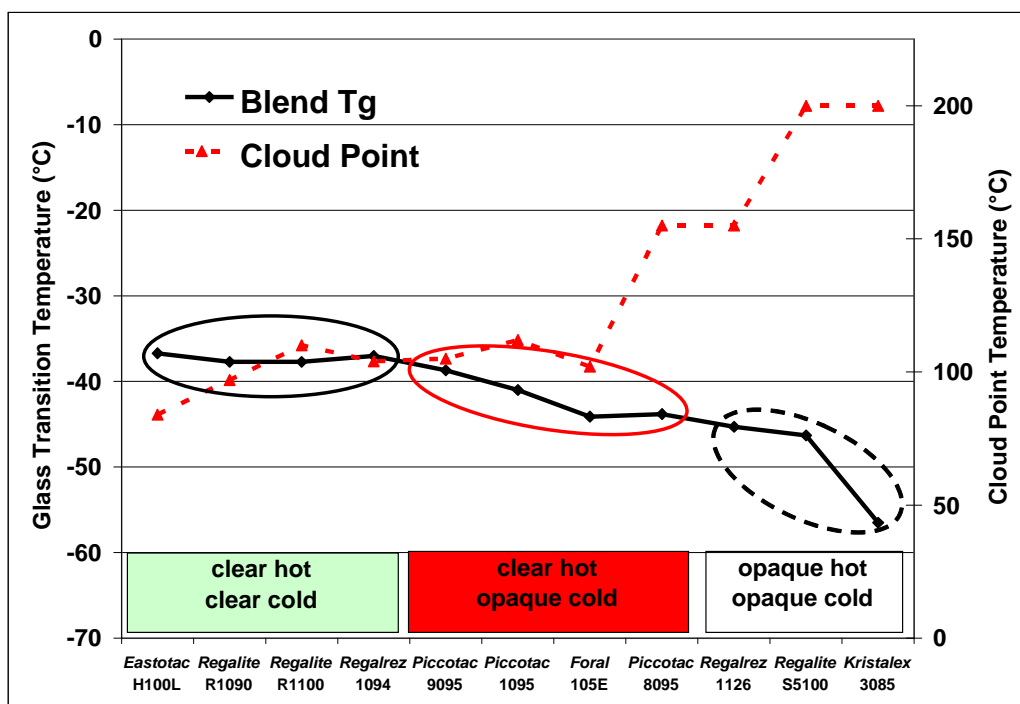


Figure 8 - Full cloud point temperatures of 1:1 OBC:tackifier blends.

Oil Compatibility Screening

To investigate the compatibility of OBC with different types of oil (mineral, paraffinic, naphthenic), the oils listed in Table 2 were compounded with OBC A and tackifier resin *Eastotac* H-100L in the proportions 100/110/10 phr.

The compounded adhesive was characterized by Ring and Ball Softening Point and Dynamic Mechanical Analysis, then coated as tape and tested for loop tack on stainless steel. Adhesives with all six oils had equivalent RBSP, but the adhesive Tg and storage modulus (G') varied significantly, as shown in Table 4. This variation was reflected in the measured loop tack values. A comparison of the loop tack values, normalized to the highest tack obtained with the 100/110/10 formulation, is presented in Figure 9. It is clear that the hydrotreated paraffinic oils such as *ParaLux* 6001 and *Hyprene* P100N were more effective at lowering the adhesive Tg and improving loop tack performance.

Table 4 - Properties of adhesives formulated with different oils at 10 phr.

Oil	Kaydol	Calsol 5550	Hydrobrite 550	Hyprene P100N	ParaLux 6001	Hyprene 60
R&B softening point (°C)	120	119	118	119	119	119
DMA - G' at 25C x10E5 (Pa)	10.0	5.0	5.5	5.8	8.7	8.9
DMA Tg (°C)	0.3	2.3	2.4	-1.7	-3.7	2.3

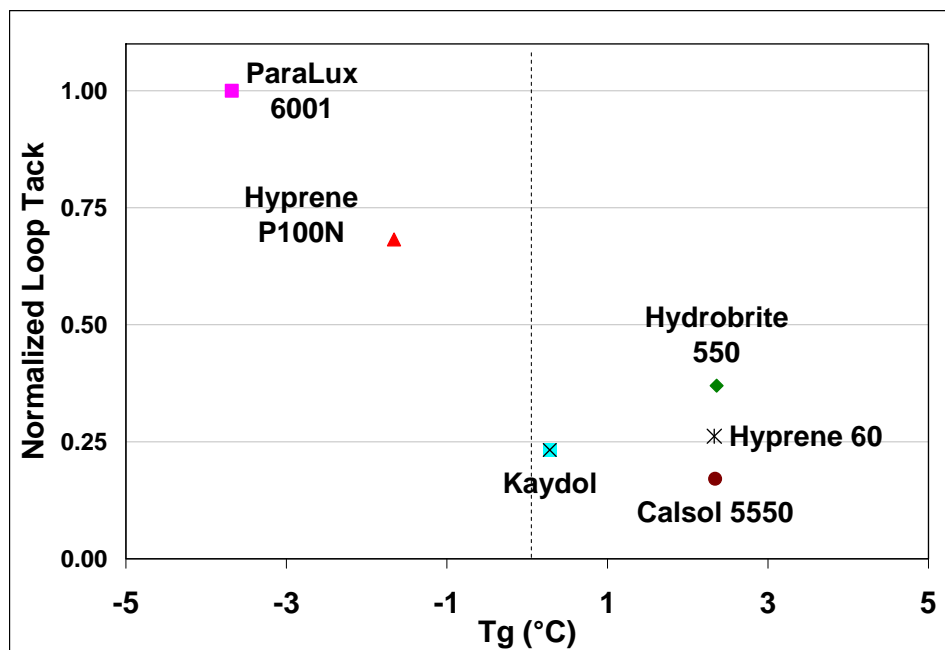


Figure 9 - Comparison of relative loop tack obtained with varying types of oils in a 100/110/10 phr formulation of OBC A/ *Eastotac* H-100L/ *Hyprene* P100N.

Tapes of the formulations prepared with *Kaydol* and *Hyprene* P100N were examined with atomic force microscopy. From the phase image, the observed morphology of the *Kaydol* adhesive showed good dispersion of the adhesive components, as shown in Figure 10. In contrast, the phase image of the adhesive containing *Hyprene* P100N showed the formation of phase-separated domains, similar to those found in styrene block copolymer adhesives, as observed in Figure 11. In comparing the height and phase images together, the *Hyprene* P100N adhesive showed that the soft domains were raised to the surface. It is hypothesized that the exposure of these soft tackified domains at the surface led to a higher level of tack.

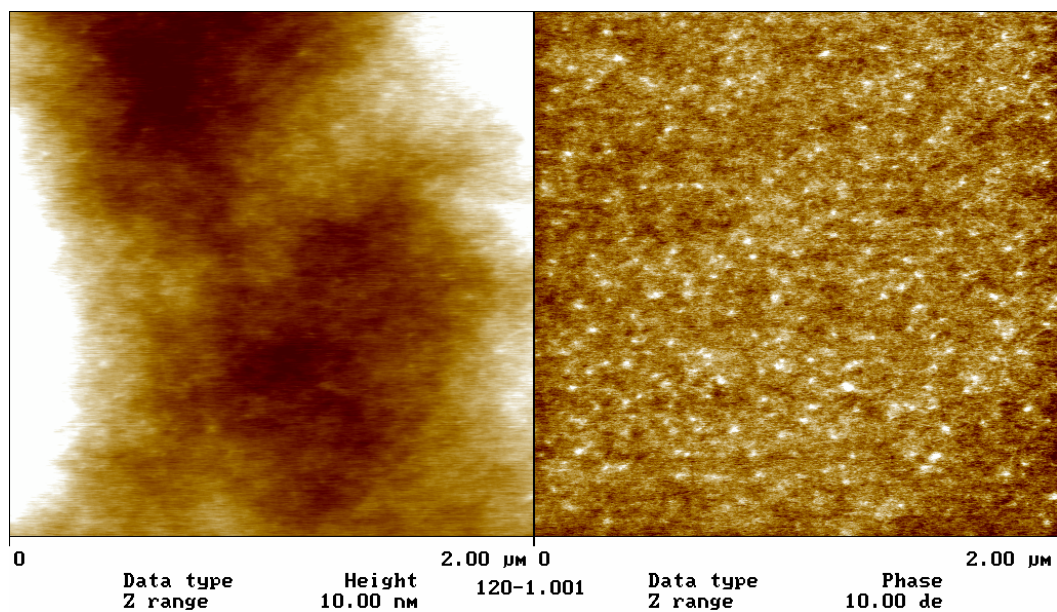


Figure 10 - AFM image of adhesive with *Kaydol* shows raised regions of harder material. White regions in the height (left) image indicate higher areas. White regions in the phase (right) image indicate harder material.

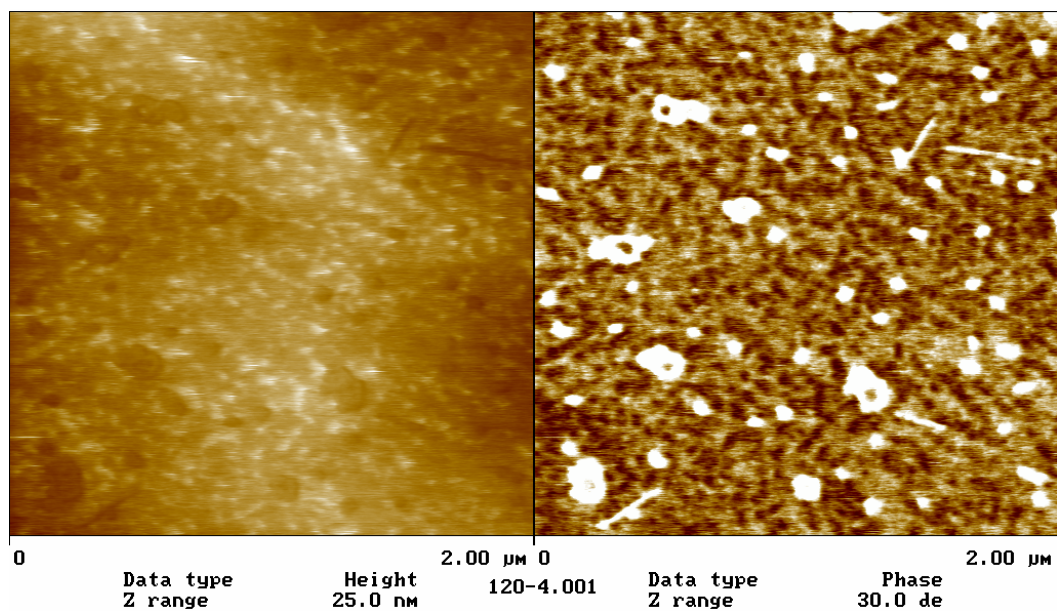


Figure 11 - AFM image of adhesive with *Hyprene P100N* shows raised regions of softer material. White regions in the phase (right) image indicate harder material.

OBC-based PSA Formulation Space

To explore the design space of OBC-based PSA's, a DOE mixture design was constructed using Design Expert 6. The experimental design space is shown in Figure 12. Fourteen runs were established with the constrained regions of:

- OBC 0.866 g/cc, 21 MI (20-45 wt%)
- Resin *Eastotac* H-100L (40-70 wt%)
- *Hyprene* P100N (10-30 wt%)

Since it was previously determined that OBC A required some oil to generate tack in the formulation, a lower limit of 10 wt% and an upper limit of 30 wt% of oil was established.

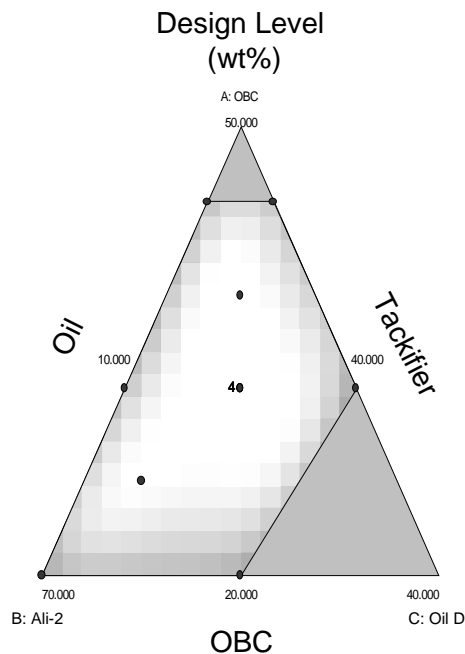


Figure 12 – Design Space for Experimental DOE with OBC/*Eastotac* H-100L/*Hyprene* P100N.

Figure 13A shows the DOE responses of the room temperature G' and Figure 13B shows the DOE response region for the PSA viscoelastic window. As shown, a wide range of G' can be achieved between 0.5 to 5.5×10^5 Pa. To achieve a G' below 2×10^5 Pa, 15 wt% oil and greater than 40 wt% tackifier is required. However, within the G' range of $0.5 - 2 \times 10^5$ Pa, the observed glass transition temperatures were within a range of 6 to -25°C . Compared to SBC's, the amount of oil and tackifier required to reach the PSA window is significantly higher due to 1) the higher room temperature G' of the OBC and 2) partial compatibility with the tackifier.

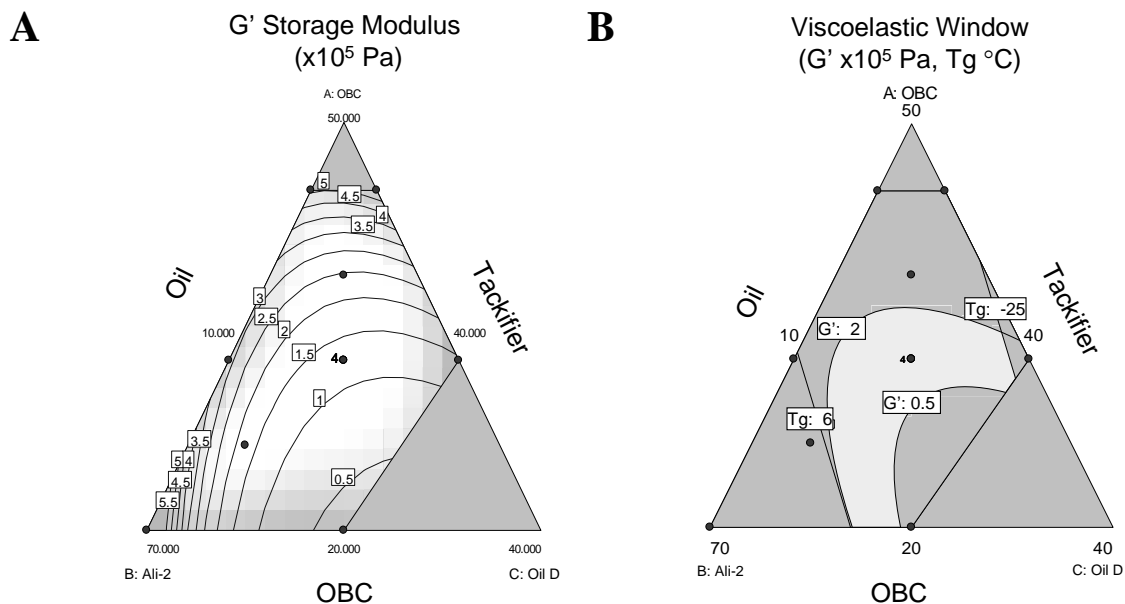


Figure 13 – G' Storage Modulus Response (A) and PSA Viscoelastic Window (B) from DOE with OBC A.

Figure 14 shows the loop tack response from the DOE of the formulated OBC's superimposed on the PSA viscoelastic window. It was observed that the tack significantly increased with oil content. It is predicted for these formulated OBC's that a range of loop tack between 40-95 oz can be achieved. From these results, it shows that a minimum of 15 wt% oil is required to generate low to moderate tack (40-50 oz). From examination of the contour lines, a non-linear response in loop tack was observed at the different levels of polymer, tackifier, and oil.

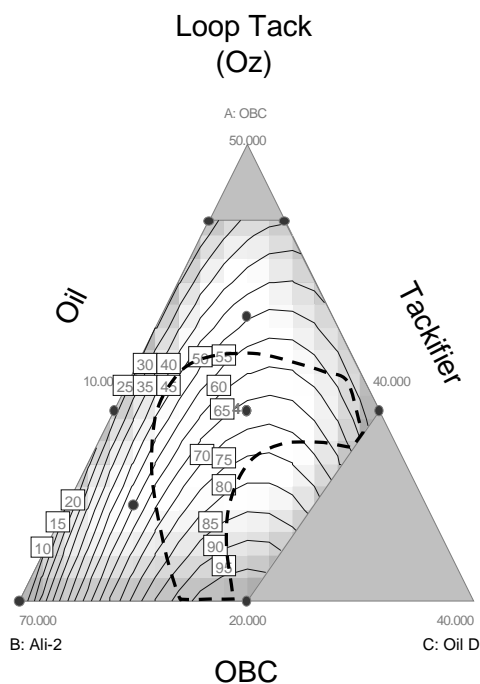


Figure 14 – Loop Tack Response from DOE with OBC A, *Eastotac H-100L* and *Hyprene P100N*.

Figures 15A and 15B show the SAFT and softening point response from the DOE of the formulated OBC's superimposed on the PSA viscoelastic window. Overall, the highest SAFT achieved was 95°C. Within the viscoelastic window, a range of 55 to 90°C is predicted and as the oil content increases, the SAFT decreases. Unusually, the predicted RBSP values remained high and between 100-112°C. In general, a good correlation between SAFT and RBSP is expected. The difference may be related to characteristics of the PSA in shear and compression modes.

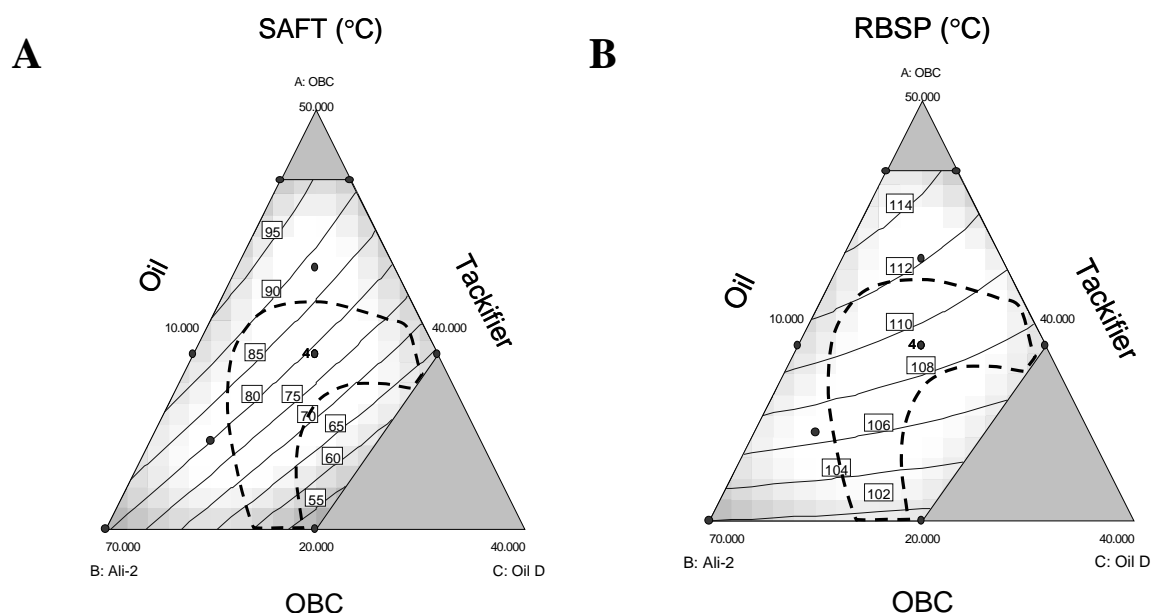


Figure 15 – SAFT (A) and Softening Point Response (B) from DOE with OBC A.

Overall for PSA formulations made with OBC A the following range of properties are predicted:

- Glass Transition: 6 to -25°C
- Loop tack range: 40-95 Oz
- SAFT (500g): 55-90°C
- R&B Softening Point: 102-112°C

Actual OBC PSA formulations tested from this design equaled or exceeded the model predictions.

OBC PSA Applications

The introduction of OBC's, as a raw material for hot melt PSA's, offers adhesive formulators a cost-effective alternative to the use of SBC's which have recently experienced significant volatility in both price and availability. OBC's can be formulated with traditional tackifiers using similar strategies to SBC's.

It was observed for the developmental OBC's tested here, that their high stiffness requires significant amounts of oil and tackifier in the formulation to enter into the PSA window. The achievable properties in the DOE show promise for certain hot melt tape and label adhesives that require moderate loop tack and SAFT.

Initial evaluation of OBC-based label formulations showed excellent processability and enhanced thermal stability when compared to SBC's. As expected due to their olefinic nature, OBC's have excellent die cutting properties.

OBC's have also been evaluated in nonwoven construction adhesives and feminine care positioning adhesives. OBC's can be blended with or substituted for SEBS in positioning adhesives without reducing peel adhesion and without transferring to the undergarment, as shown in Figure 16.

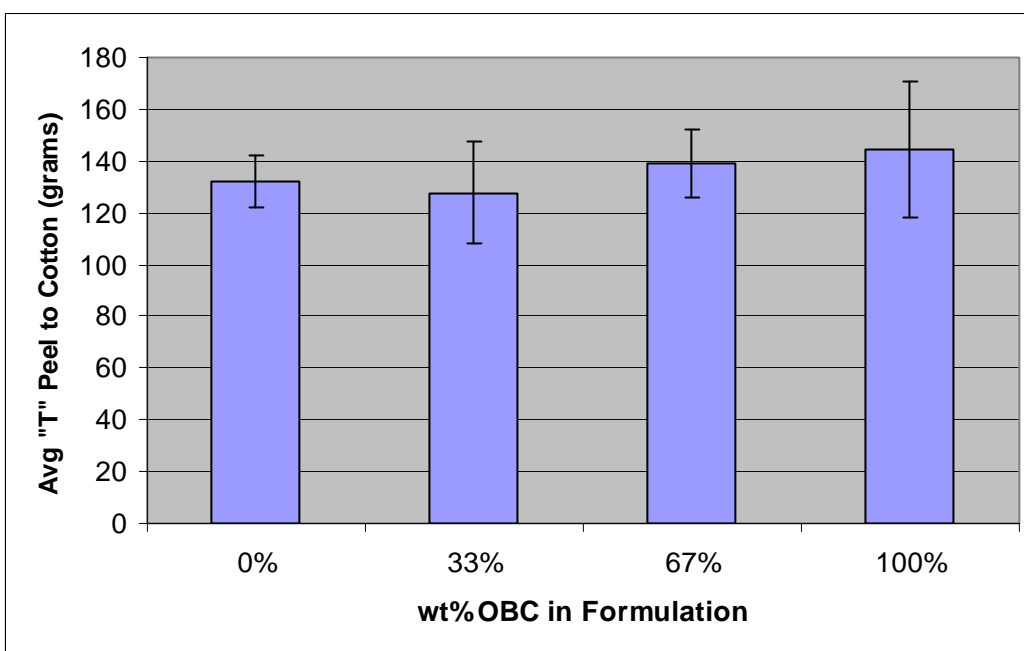


Figure 16 – SEBS/OBC Positioning Adhesive Testing

Although the first generation OBC's tested were unoptimized for pressure sensitive adhesive applications, the results of this study have provided insight into the future design of OBC polymers for PSA's. Future evaluation will include OBC's which will be specifically designed to address the needs of adhesive markets.

Conclusions

The introduction of OBC's for hot melt PSA's offers an alternative polymer that can be formulated with traditional tackifiers using similar strategies to SBC's. Similar to other polyolefins, OBC-based PSA's have the advantage of excellent processability and enhanced thermal stability.

It was found that the tackifier and oil relationships for OBC's are unique and careful selection is required when developing OBC PSA's. The tackifier and oil requirements for OBC's were found to be:

- OBC's are most compatible with fully hydrogenated tackifiers regardless of the chemical class. Fully hydrogenated tackifiers with molecular weights less than 2500 g/mol are recommended. The hydrogenated hydrocarbon resins *Eastotac* H-100L, *Regalite* R1090 and R1100, and *Regalrez* 1094 are preferred for use with the OBCs tested here.
- OBC's exhibited an unexpected sensitivity to the oil type where hydrotreated paraffinic oils were most effective in generating tack.

The developmental OBC's tested here had high stiffness and required significant amounts of oil and tackifier in the formulation to enter into the PSA window. PSA formulation design showed that a moderate range of loop tack and SAFT's can be obtained.

Overall, the results of this study have provided insight into the design of future OBC polymers to address the needs of adhesive applications.

Acknowledgements

We would like to thank our colleagues for helping with the PSA testing and support especially, Tim Williams, Lois Taylor, Jill Wilson, Deborah Moroney, Jim Allen, Bobbi Guillbeaux, and Dr. Mark Peters.

References

1. Patent publications WO2005090427, WO2005090426, WO2005090425, US2006199930A1
2. Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T.; *Science*, 5, 714-719 (2006).
3. Hiltner, A.; Wang, H.; Khariwala, D.; Cheung, W.; Chum, S.; Baer, E.; SPE Annual Technical Conference 2006, Charlotte, May 7-11, 2006.
4. Karande, S.; SPE Annual Technical Conference 2006, Charlotte, May 7-11, 2006.
5. Dahlquist, C.A. *Pressure-Sensitive Adhesives*; Patrick, R.L., Ed.; Dekker, 1969; Vol. 2, 219-260.
6. Chu S.G.; "A New Reinforcing Resin for Kraton Block Copolymers"; Proceedings Adhesives and Sealants Council Meeting 1984.
7. Foley, K.F. and Chu, S.G.; *Adhesives Age*, 29, 24-28 (1986).

8. Fox, T.G.; *Bull. Am. Phys. Soc.*, 1, 123 (1956).