

ELUCIDATION OF MODULUS AND RHEOLOGICAL PROPERTIES OF AMBIENT CURE PSA EMULSIONS

Raj Hariharan, Sr. Group Leader

Vinavil Americas

Deerfield Beach, FL 33442



Dr. Raj Hariharan is a Sr. Group Leader with Vinavil Americas, a MAPEI Corporation, where he works on research, development, production and application of PSA adhesive products for flooring, label and other related industries. Before Joining MAPEI, Raj worked for Rohm and Haas/Dow Chemical. Raj has a Ph.D. in Polymers from Baylor University, TX, USA. He has authored several United States and International patents, and published several articles in peer reviewed journals.

Abstract:

Ambient cure Pressure Sensitive Adhesive (PSA) emulsions play a big role in permanent and temporary adhesive label applications in coater ready PSAs. The main focus of this study is to correlate modulus properties such as peel and tack attributes of various ambient cure PSA emulsions. An attempt is also made to understand viscoelastic behavior of ambient cure emulsions and explain how it could be correlated to modulus and performance characteristics. Focus on environmental and sustainability advantages of PSA emulsions are also elucidated while maintaining critical performance attributes.

Introduction

The process for producing pressure sensitive adhesive (PSA) coated labels currently used by the industry consists of applying a solvent based or aqueous based PSA to a low energy surface (release sheet) using a suitable coating process such as gravure, slot die coating followed by drying the adhesive and transferring the dry adhesive to the label stock by laminating the adhesive coated release sheet to the back surface of the label stock. The face of the label may be printed by conventional printing technologies. The label is then die cut to predetermined dimensions and sold for commercial use.

To apply the label to a substrate, the label is first removed from the release sheet, the adhesive now bonded to the back side of the label and the adhesive coated side of the label pressed onto the substrate. In order for the adhesive coated label to cleanly be removed from the release sheet, the surface energy of the release sheet must be significantly lower than the surface energy of the adhesive. For typical polyacrylate ester adhesives, the surface energy is about 28 to 35 dyne/cm. A preferred release sheet is a polydimethyl siloxane (silicone) coated web with a surface energy is about 22 dyne/cm.

The application of solvent based PSA's to release sheets presented little to no problem to the industry because the surface tension of such adhesive solutions was about 20 to 25 dyne/cm, low enough to provide good wetting of the release sheet. Driven by health and environmental pressures and the cost of organic solvents, the industry has increasingly turned to alternatives such as 100% solids PSAs and waterborne PSAs. Currently, water-borne adhesives are the adhesive of choice because 100% solids PSA's lack the balance of adhesive performance characteristics required by the label industry.

With the growth of major industries such as Consumer Goods, Healthcare, Automotive and Electronic Goods, the Global adhesive Label market is set to grow at a CAGR of 3.8-4.5 % (1) in terms of volume and revenue of a total Global market size of >1.5 B. The aqueous products are predicted to enjoy tremendous growth due to environmental and other health restrictions as well as general acceptability by the market place (1).

When switching over to aqueous emulsions, industries do not want to compromise on the performance attributes of the label products. So it is imperative to maintain excellent performance attributes such as peel, shear properties while maintaining the flexibility of use on multitude substrates (2).

Rheological properties of aqueous PSAs reflect the deformation or flow of emulsion polymers subjected to shear forces. Rheology has significant effects on emulsion polymers due to formulation, storage and transportation as well as use of these products in final coating applications including substrate wetting and drying to form the end use pressure sensitive adhesive film (3, 4).

Materials and Experimental Description - Coater Ready Emulsions Study

Aqueous based Coater Ready Emulsions (CRE) are typically formulated from latex polymers to exhibit desired properties depending on the type of application. In this study, two types of CREs were investigated, one is for permanent label application for a wide variety of substrates and the other for

clear permanent label application that can be applied to clear substrates. The properties desired for these applications can be challenging and thus require appropriate emulsion polymers that will enable to achieve desired properties. The main advantage of aqueous based CRE is that they are environmentally friendly with little to no volatile organics. The latex is typically formulated with defoamers and air release agents to prevent excess foaming during the manufacture and web coating process. Formulations may also include thickeners and pH adjusters to achieve desired rheological properties. They are also formulated to have desired levelling, adhesion and thermal properties, to have uniform defect free coating and provide stability upon heat and air drying to form a uniform PSA film .

Sample Preparation, Instrumentation and Test Methods

Since application dictates appropriate viscosity and rheological property range, latex polymers by themselves are not readily usable and need to be formulated. Latex polymers were formulated into products suitable for the end use applications using standard formulary equipment. Formulations were typically made in lab scale and properties such as pH, solids and viscosities were measured using standard equipment using established procedures.

Formulations were prepared and were allowed to equilibrate at ambient temperature $70 \pm 2^\circ\text{F}$ for more than 24 h before further use. Coating substrates and materials were allowed to equilibrate at $70 \pm 2^\circ\text{F}$ and $50 \pm 2\%$ relative humidity and all tests were also performed at this condition. Samples were drawn down using standard Mayer coating rods. Loop tack peel was tested according to Standard Test Method for Loop Tack, PSTC-16 using Texture Technologies. Peel adhesion was tested according to the ASTM D 3330 method using Instron. Rheological properties were measured using Anton Paar MCR 3 Rheometer with PP25-SN20093, PP gap $d=1\text{mm}$. Viscosity measurements were performed using Brookfield viscometer with appropriate spindle and speeds. DSC measurements were performed using DSCi instrument. Ramp rates were $20\text{C}/\text{min}$ using Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry ASTM D3418.

Results and Discussion

CRE were formulated from emulsion polymers depending on the type of applications and are summarized in **Table 1**. The first type of CRE is used for permanent label applications on wide variety of substrates. The second type of CRE is used for clear label applications. Emulsion VC-L1 is an unformulated latex that was formulated to be coater ready as CRE-L1 used for permanent label application. CRE-L2 was a commercial formulated CRE, which was used in this study for benchmarking comparison. Similarly, VC-L2 was an unformulated latex and the corresponding formulated emulsion was CRE-CL.

Table 1 Coater Ready Emulsions (CRE) Description and Properties

Latex	Type	T _g , °C*	Viscosity, cP	Solids, %	Application
VC-L1	Emulsion-1	-40	600	>55	Unformulated Latex
CRE-L1	Permanent Label-L1	-43	460	56	Formulated Permanent Label Adhesive
CRE-L2	Permanent Label -L2	-48	550	58	Formulated Permanent Label Adhesive
VC-L2	Emulsion-2	-38	60	55	Unformulated Latex
CRE-CL	Clear Label-CL	-35	600	56	Permanent Clear Label

* T_g, °C, measured by DSC

It can be observed from **Table 1** that CRE-L1 has a lower T_g compared to unformulated emulsion. An example of thermal analysis using DSC in measuring T_g is shown in **Figure 1**.

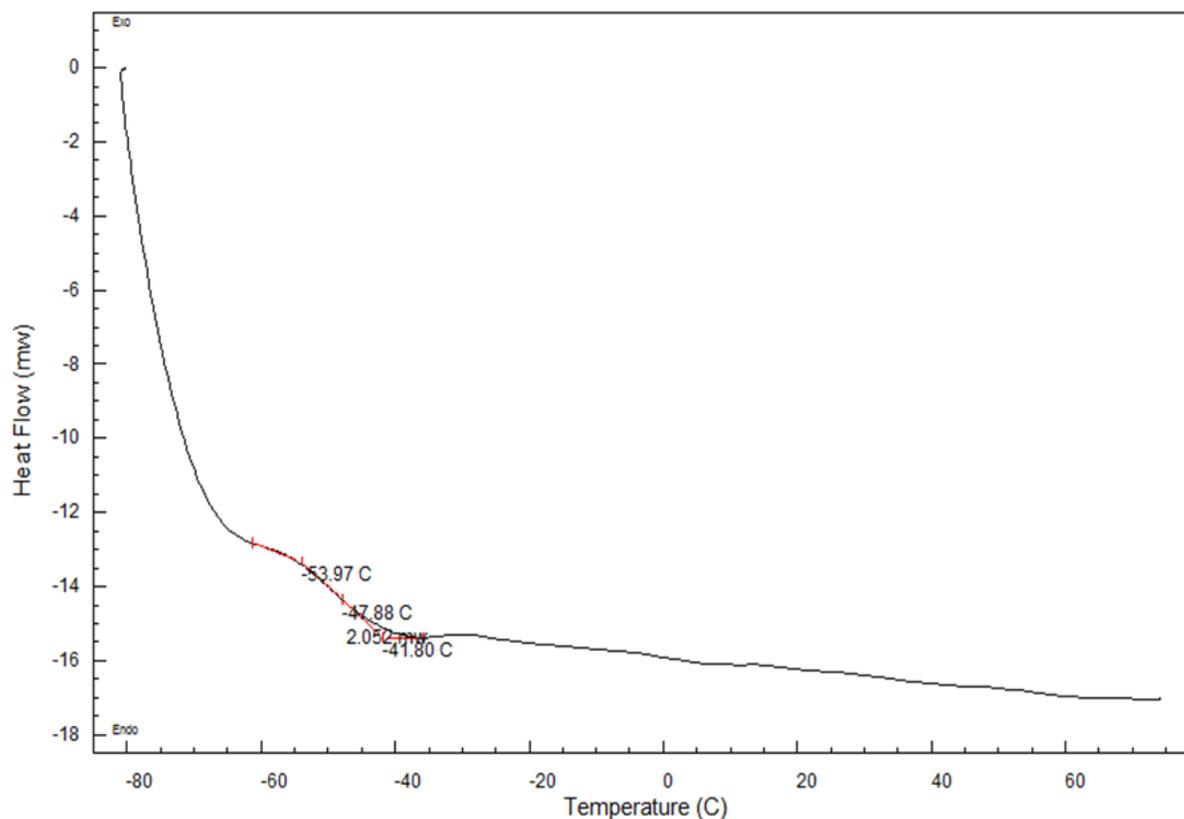


Figure 1 DSC Thermal Analysis of CRE-L2

Table 2 shows comparison of loop tack properties of permanent label CRE-L1 and CRE-L2. Both CRE-L1 and CRE-L2 have good tack properties on difficult to adhere substrates such as HDPE,

polypropylene and Tyvek® substrates. It can be observed that CRE-L1 has a higher loop tack compared to CRE-L2, for different substrates. The failure modes for all substrate were adhesive.

Peel properties for CRE-L1 and CRE-L2 are compared in **Table 3** for different substrates along with their failure modes. It can be observed that CRE-L1 shows paper tear for all substrates exhibiting excellent adhesive strength characteristics. It also exhibits failure of corrugated board and Tyvek®, which are much desired properties of adhesion to these substrates.

Table 2 Loop Tack Properties of Permanent Label, CRE-L1 and CRE-L2

Substrate	CRE-L1, PSI*	CRE-L2, PSI*
Stainless Steel(SS)	3.7	2.8
Glass	3.0	2.9
Corrugated Board	2.3	2.3
Tyvek®	1.5	1.5
HDPE^	3.1	3.0
Polypropylene	4.1	3.0

*PSI: Lb/Sq.in.; Failure mode: Adhesive

^High density polyethylene

Table 3 Peel Properties* comparison of Permanent Label, CRE-L1 and CRE-L2

Substrate	CRE-L1, PLI^	Failure Mode	CRE-L2, PLI^	Failure Mode
SS @ 180 Degree	3.0	Paper tear	2.6	Adhesive
Glass @ 90 Degree	3.0	Paper tear	2.6	Adhesive
Corrugated Board @ 90 Degree	3.5	Board tear	2.2	Adhesive
Poly Styrene @ 90 Degree	2.2	Polystyrene tear	2.2	Adhesive
Tyvek® @ 90 Degree	2.9	Tyvek failure	2.3	Adhesive

*Face stock paper dwell time with substrate was 45 min before peel test

^PLI= Lb per linear inch

Table 4 shows peel properties of CRE-CL for different substrates, which are mainly adhesive in their failure mode.

Table 4 Peel Properties* of CRE-CL for Different Substrates

Substrate	CRE-CL, PLI [^]
SS @ 180 Degree	1.3
Glass @ 90 Degree	2.5
Corrugated Board @ 90 Degree	1.8
HDPE	1.4
PET	2.3

*Face stock PET dwell time with substrate was 45 min before peel test

[^]PLI= Lb per linear inch

Rheological Studies of Permananet Label CREs

Flow and viscosity curves of latex and coater ready emulsions can be compared by plotting shear stress versus shear rate for flow behavior and viscoisty versus shear rate for viscosity behavior. **Figure 2** shows both flow and viscosity curves comparing VC-L1, unformulated latex with CRE-L1 formulated coater ready emulsion.

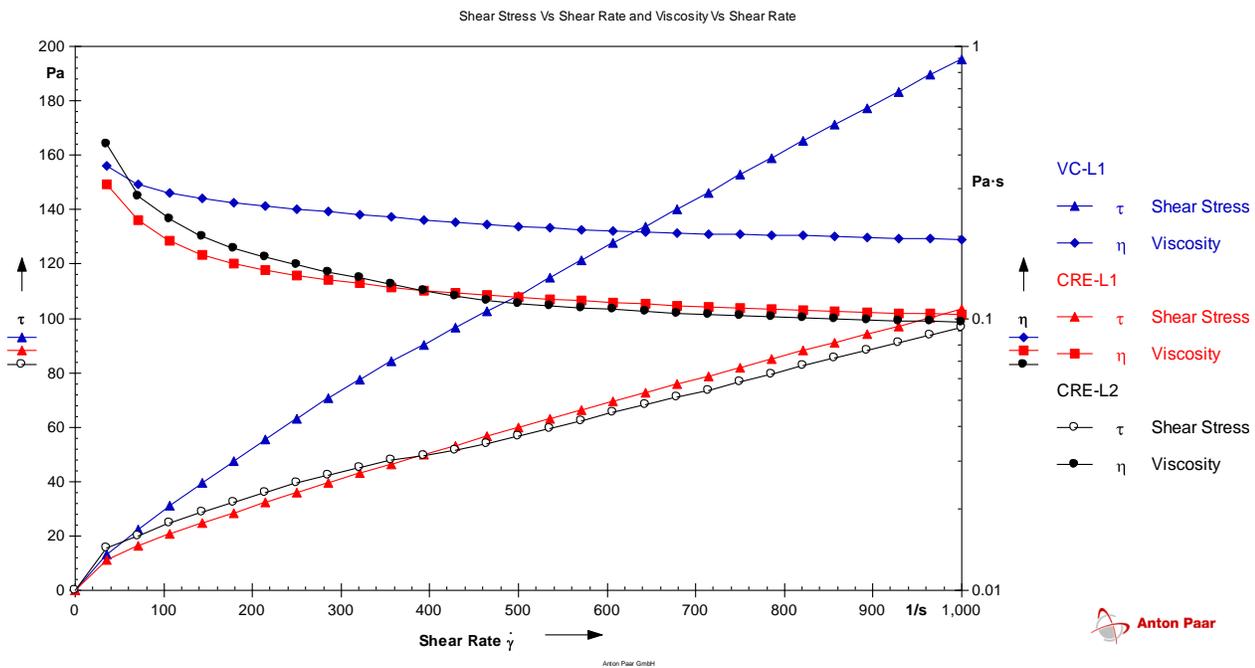


Figure 2 Flow Curve (Shear stress versus shear rate) and Viscosity Curve (Viscosity versus shear rate) of CREs for Permanent Label Applications

It can also be observed from **Figure 2** that CRE-L1 shows lower yield stress compared to unformulated latex. VC-L1 and CRE-L1 show an yield point of 11 Pa and 13 Pa, respectively at 36 sec⁻¹ shear rate. CRE-L2 has yield stress point of 15 Pa at 36 sec⁻¹ shear rate. All emulsions exhibit shear

thinning, pseudo plastic behavior over the entire shear rate (4, 5). From a rheological point of view, a yield point is the lowest shear-stress value above which a material will behave like a viscoelastic fluid, and below which the material will act like a viscoelastic solid (6, 7).

Rheometric oscillatory test can be utilized to obtain more insight into the viscoelastic behavior of these materials. Amplitude sweep aims at describing the deformation behavior of samples in the non-destructive deformation range. It also helps in determining the upper limit of this range. In the shear-strain amplitude sweep, with controlled-shear deformation (CSD) mode, Linear Viscoelastic (LVE) region can be determined where the range in which the test can be carried out without destroying the structure of the sample. LVE region is also defined as lowest strain value or a tolerance range of deviation for storage modulus, G' plateau value.

Figure 3 shows comparison of controlled-shear stress deformation (CSD) pattern of coater ready emulsions, CRE-L1 and CRE-L2. **Figure 4** shows comparison of controlled-shear stress (CSS) Study of label emulsions CRE-L1 and CRE-L2. **Table 5** summarizes linear viscoelastic parameters and storage and loss modulus G' and G'' , respectively for coater ready permanent label emulsions.

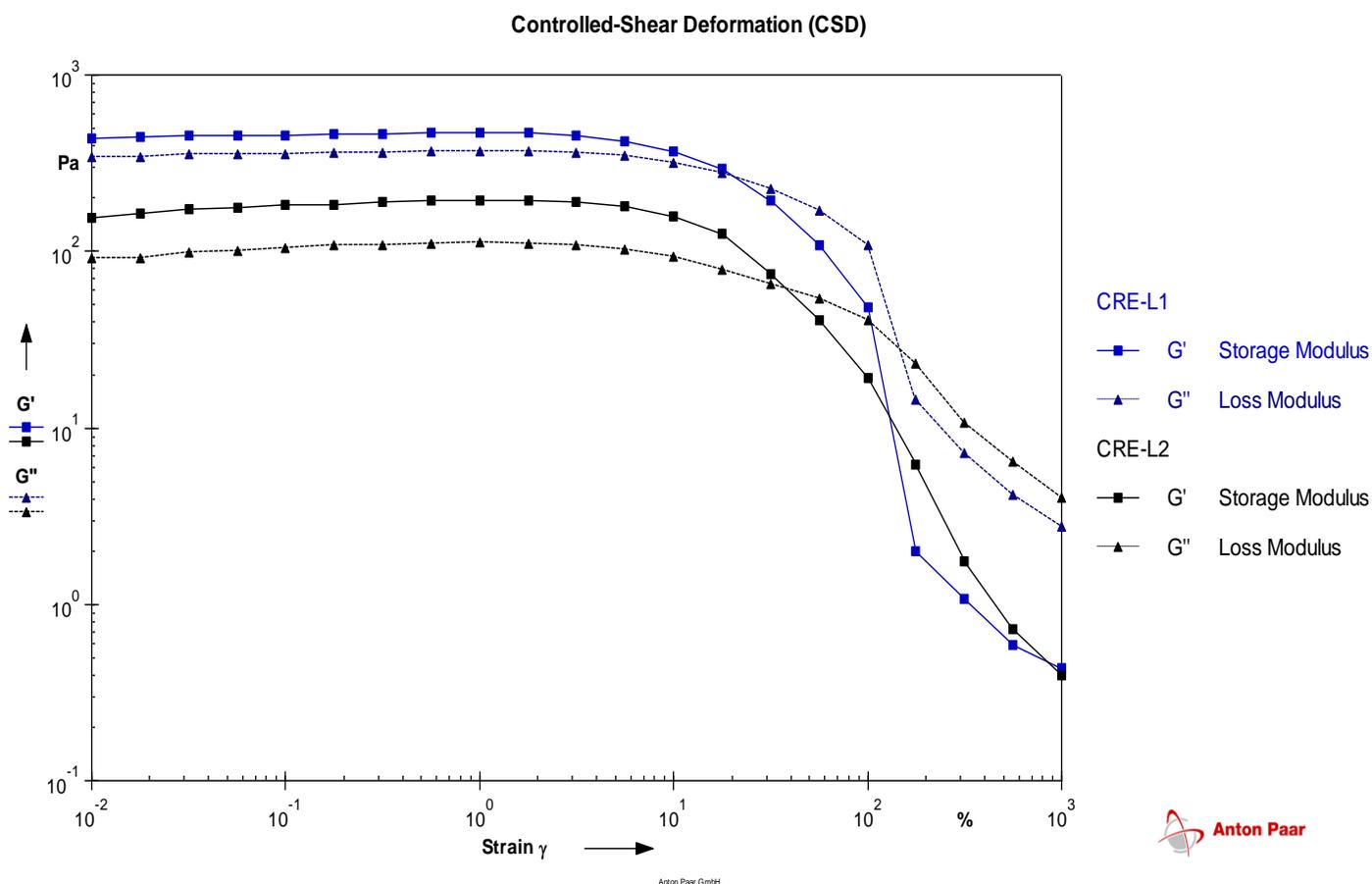


Figure 3 Controlled-Shear Deformation Study Comparisons of Label Emulsions CRE-L1 and CRE-L2

Table 5 Linear Viscoelastic Range and Modulus Values of CRE Permanent Label Emulsions

Latex	Type	% Strain (γ_L) ¹	LVE ² , YP ³ , Pa	FP ⁴ , G'=G'', Pa	G', Pa	G'', Pa
VC-L1	Emulsion-1	1	12	95	540	374
CRE-L1	Coater Ready Emulsion-1	1	11	72	468	366
CRE-L2	Coater Ready Emulsion-2	1	2.2	31	192	110

(γ_L)¹ = Linearity limit strain; LVE²=Linear Viscoelastic Region

YP³ = Yield Point; FP⁴ = Flow Point

It can be observed that linearity limits strain γ_L of all CRE are about 1%. This is the maximum deformation value at or below which oscillatory studies can be carried out by keeping the internal structure of the sample intact. Yield point or yield stress is the value of shear stress at the limit of the LVE region. Fluid point or flow stress, is the value of shear stress at the cross over point of G' and G'' i.e., G'=G''. The yield point and flow point of CRE-1 is slightly lower than the corresponding unformulated emulsion VC-L1. Comparison of YP, FP, G' and G'' for CRE-L1 and CRE-L2 shows that for CRE-L1, the values are higher than CRE-L2. Below the flow stress point (left part of curve in **Figure 3**) both CRE-L1 and CRE-L2 behave gel-like, viscoelastic solid character and above the flow stress point they behave more fluid-like, viscoelastic fluid. The flow stress point for CRE-L1 is greater than CRE-L2, which may indicate that under higher coating stress conditions, CRE-L1 will be a more stable emulsion and will operate more smoothly without formation of much grit over a wide web. The higher G' for CRE-L1 compared to CRE-L2 shows CRE-L1 has more cohesive strength than CRE-L2, which could explain higher loop tack peel and peel strength for CRE-L1 compared to CRE-L2 as observed in **Tables 2** and **3**, respectively.

Frequency sweeps generally serve the purpose of describing the time-dependent behavior of a sample in the non-destructive deformation range. Conventionally frequency sweeps are proven method for gathering information on the inner structure of polymers and long-term stability of emulsion polymers. In this study CREs were also compared using frequency sweep test, which was performed at 1% strain level. Strain γ_L was obtained from controlled shear deformation amplitude studies as discussed earlier. **Figure 5** shows frequency sweep comparison of CRE-L1 and CRE-L2. At this deformation (strain) value of 1%, the emulsions behave more viscoelastic solid as indicated by G'>G''. From **Figure 5** it can be observed that G' and G'' for CRE-L1 is greater than CRE-L2, which confirms the higher peel strength that was observed for CRE-L1 compared to CRE-L2. It is also interesting to note from **Figure 5** that the complex viscosity, η^* for CRE-L1 is higher than CRE-L2. In contrast, viscosity curves of CRE-L1 and CRE-L2 in **Figure 2** were not significantly different from each other. Since η^* is a function G*, complex shear modulus, $\eta^* = G^*/\omega$, where ω is the angular frequency. This further indicates that G* for CRE-L1 is higher than CRE-L2.

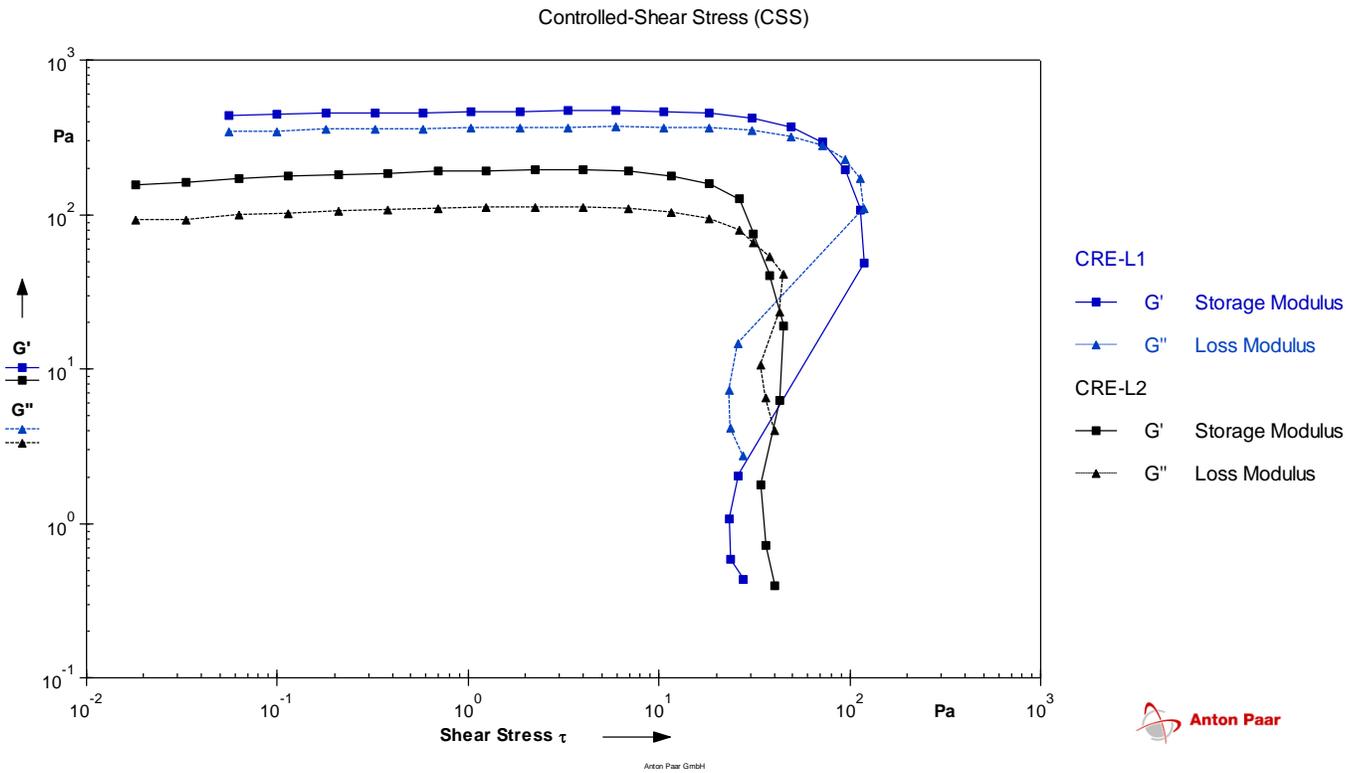


Figure 4 Controlled-Shear Stress (CSS) Study Comparisons of Label Emulsions CRE-L1 and CRE-L2

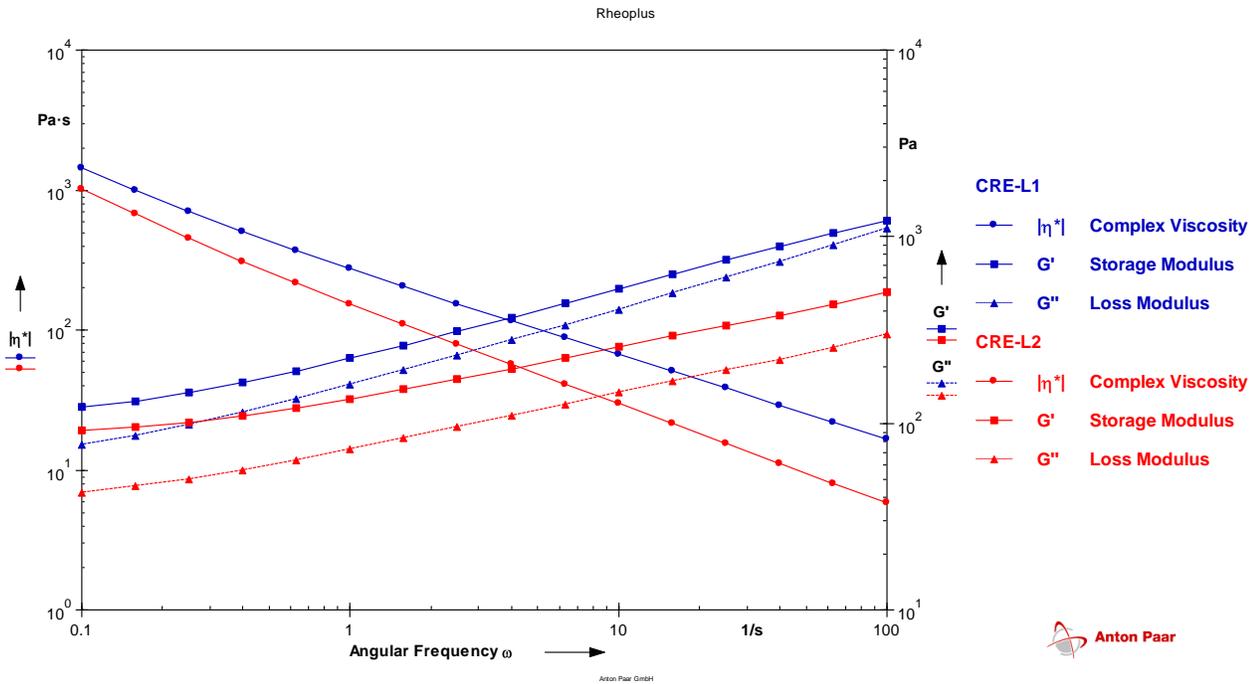


Figure 5 Frequency Sweep Comparison of Label Emulsions CRE-L1 and CRE-L2

Rheological Studies of Clear Label Coater Ready Emulsions

Figure 6 shows comparison of flow and viscosity curves of unformulated and formulated latex emulsions VC-L2 and CRE-CL, respectively for clear label applications. It can be observed that the yield point of unformulated latex is 1.5 Pa compared to formulated latex emulsion CRE-CL of 66 Pa at 36 sec^{-1} shear rate. All emulsions exhibit shear thinning, pseudo plastic behavior over the entire shear rate.

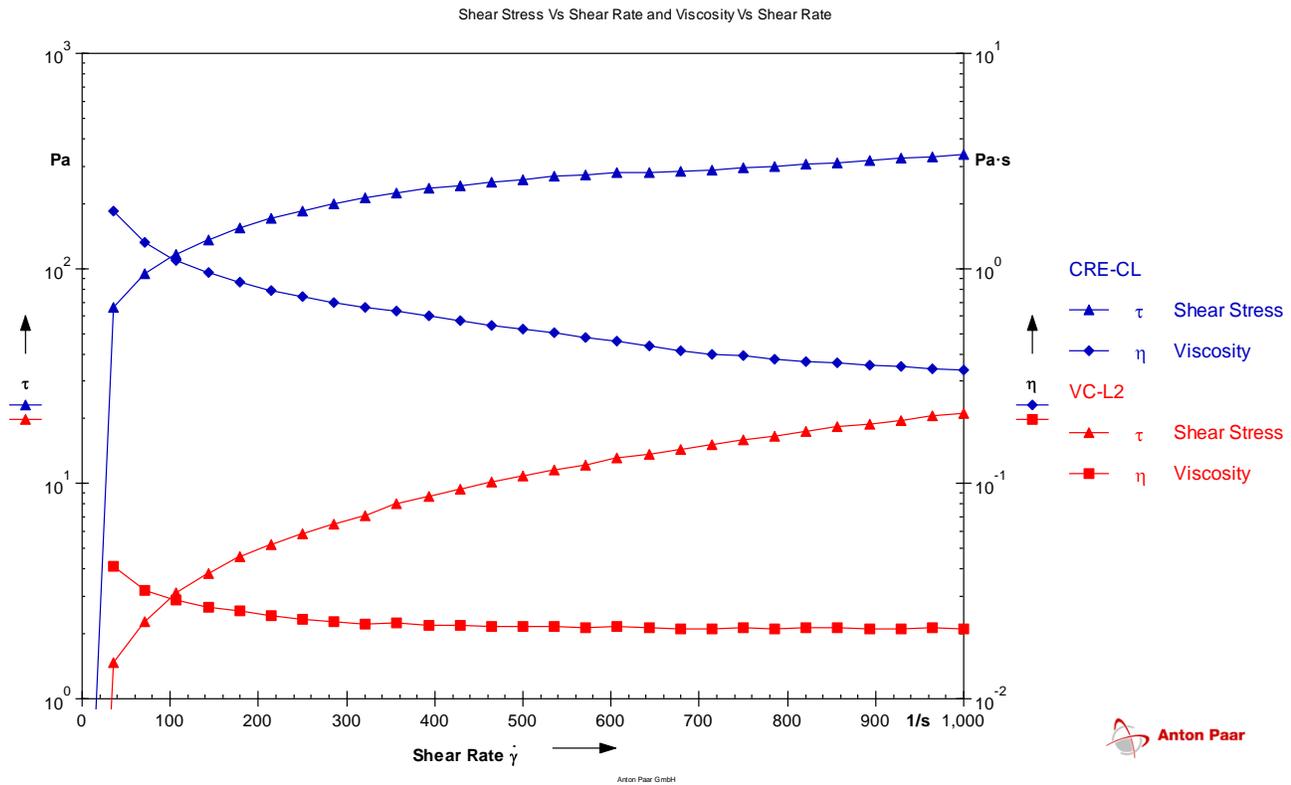


Figure 6 Flow Curve (Shear stress versus shear rate) and Viscosity Curve (Viscosity versus shear rate) of CREs for Clear Label Applications

Table 6 Linear Viscoelastic Range and Modulus Values of Clear Label Coater Ready Emulsions

Latex	Type	% Strain (γ_L) ¹	LVE ² , YP ³ , Pa	FP ⁴ , $G'=G''$, Pa	G' , Pa	G'' , Pa
VC-L2	Emulsion-1	0.18	0.10	0.45	31	10
CRE-CL	Coater Ready Emulsion-1	1.8	7.5	99	367	210

(γ_L)¹ = Linearity limit strain; LVE²=Linear Viscoelastic;

YP³ = Yield Point; FP⁴ = Flow Point

Figure 7 shows comparison of controlled-shear stress deformation (CSD) pattern of formulated clear label coater ready emulsion, CRE-CL compared to unformulated VC-L2. **Figure 8** shows comparison of controlled-shear stress (CSS) study of CRE-CL compared to VC-L2. **Table 6** summarizes linear viscoelastic region parameters, storage G' and loss modulus G'' parameters, respectively for VC-L2 and CRE-CL. It can be observed that linearity limits strain γ_L of VC-L2 is ten times lower at 0.18 % compared to CRE-CL at 1.8%. As observed from the CSD and CSS curves, **Figures 7 and 8**, that the YP of LVE region and the flow stress point for CRE-CL is greater than VC-L2 showing that under higher coating shear-stress conditions, CRE-CL will be a more stable emulsion and will enable to operate more smoothly without much grit formation especially in higher shear coating operations such as gravure, slot die coating processes. **Figure 9** shows frequency sweep study comparison of CRE-CL compared to VC-L2. The sweep study was done at 1% deformation strain value for both emulsions. **Figure 9** shows that for CRE-CL, $G' > G''$ over the entire sweep showing stable viscoelastic solid behavior, whereas for VC-L2 at angular frequency > 6 rads/s, $G'' > G'$. This point where the loss modulus G'' being higher shows viscoelastic liquid nature with poor shear stability.

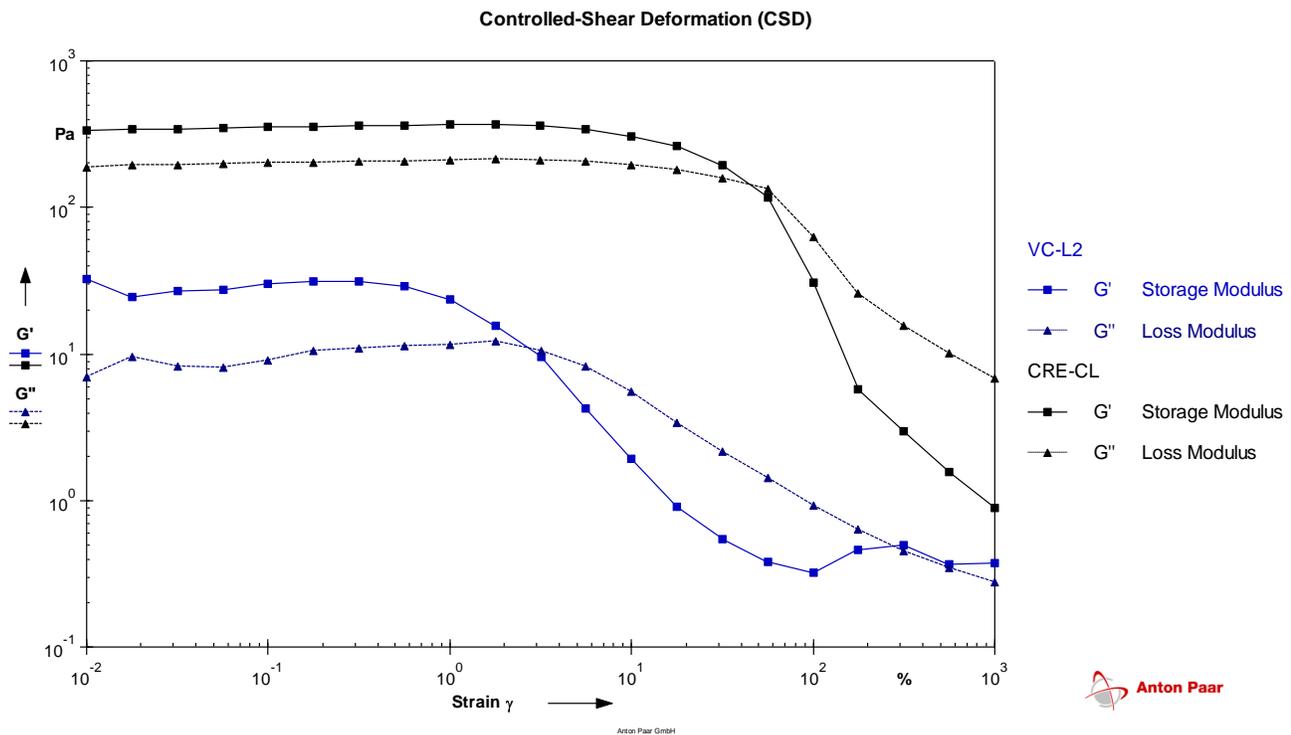


Figure 7 Controlled-Shear Deformation Study Comparisons for Clear Label Applications

Figure 9 also shows that the complex viscosity, η^* for CRE-CL is higher than VC-L2. This further indicates that G^* for CRE-CL is higher than VC-L2.

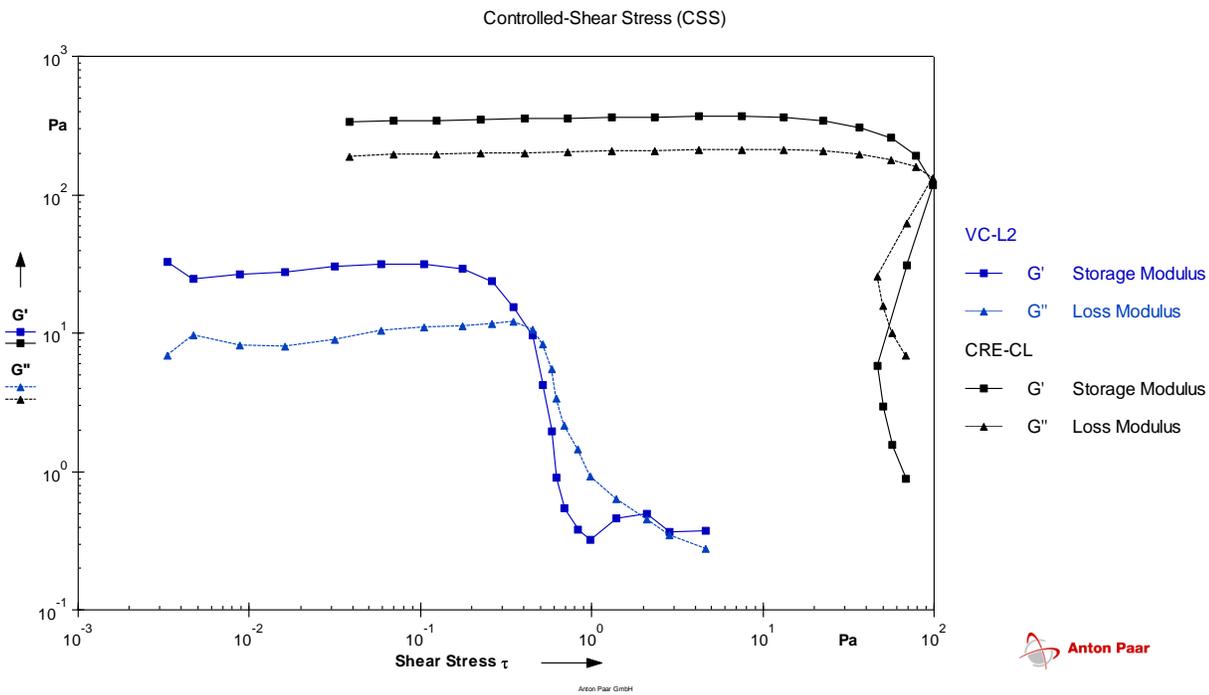


Figure 8 Controlled-Shear Stress Study Comparisons for Clear Label Application

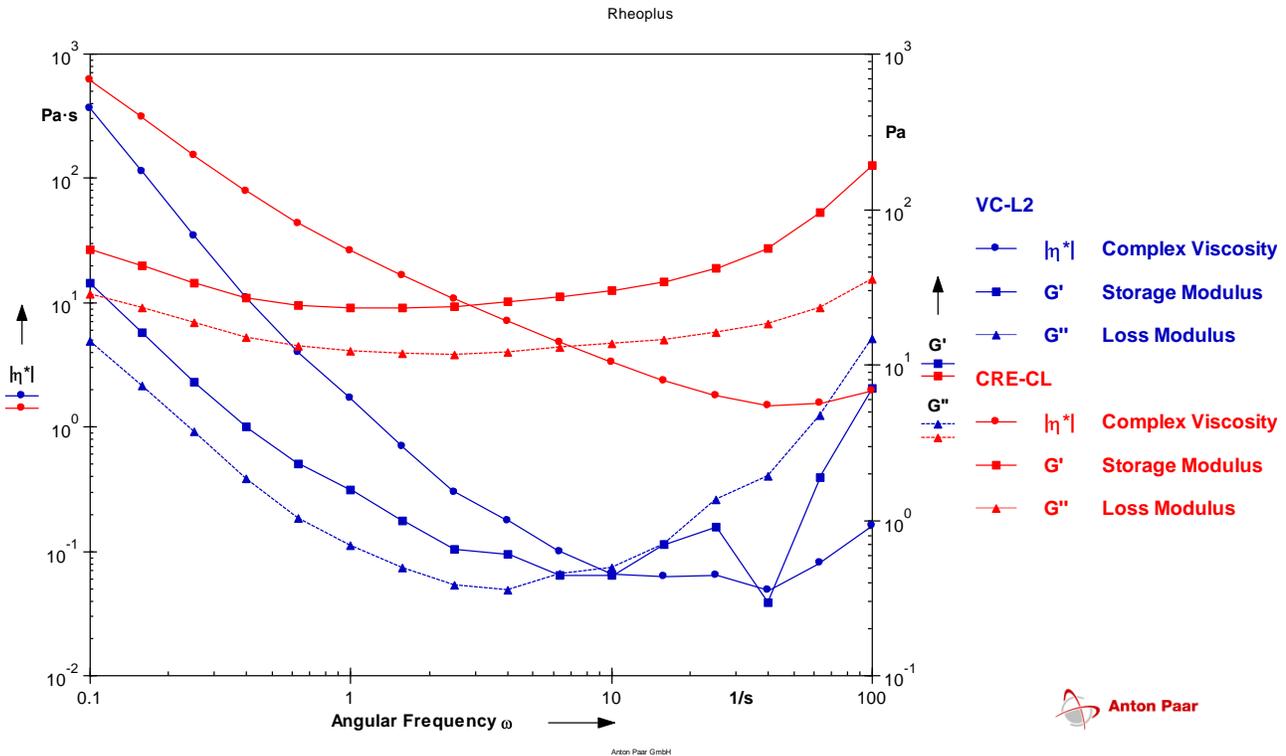


Figure 9 Frequency Sweep Comparison of Clear Label VC-L2 and CRE-CL emulsions

Environmental and Sustainability Advantages of Aqueous PSA Emulsions

There is a great deal of environmental regulations from agencies such as South Coast Air Quality Management District (SCAQM) to meet volatile organic compound (VOC) requirements (8). Living

building challenge compliant has strict regulations of limiting red list compound such as alkyl phenols in certain product applications (9, 10). Demand for environmentally friendly products are ever increasing and one of the best possible ways in meeting the demands is through aqueous PSA emulsions. PSA emulsions have great flexibility in terms of latex properties and can be tailored to meet application requirements. Various types of monomers, processing methods, and additives can be used during emulsion polymerization, making the process extremely flexible. A wide variety of products with specialized properties can be manufactured. Emulsion polymerization allows for the production of particles with specialty-tailored properties including size, composition, morphology, and molecular weight.

Significant amount of awareness is being generated regarding sustainability through usage of renewable or recyclable raw materials in adhesive products (11). This encourages green consumerism for customers. Among various materials that are available for a sustainable raw material source, bio-renewable polymers derived from different natural resources are considered as an almost inexhaustible source of sustainable materials in the world. Bio-renewable polymers can be easily obtained from abundant inexpensive renewable bio-resources and their properties of abundance, easily availability, and low cost have made them one of the most promising raw material. The bio-renewable raw-material source is gradually expected to replace at increasing levels of currently used crude oil based products.

Certain amounts of bio-renewable resource were used in some of the formulations in the current study. It was of prime importance not to compromise on the final performance requirements. Care was also taken to avoid using raw materials that may contribute significantly to volatile organic compounds (VOC) emissions thus meeting Air quality rules. The PSA emulsions in this study are void of red list compounds such alkyl phenols. All these efforts contribute towards a sustainable growth of business and corporate social responsibility while maintaining key environmental and performance attributes.

Summary

In this study, two types of coater ready emulsions were investigated one, permanent label application for a wide variety of substrates and the other is for clear permanent label application that can be applied to clear substrates. For permanent label and clear label applications loop tack and peel modulus properties were compared. It was found that the formulated permanent label PSA, CRE-L1 had better peel properties for a variety of substrates. This also agree with the loop tack properties for that particular permanent PSA label emulsion.

Rheological properties of CREs were investigated to better access the deformation and flow behavior of PSA latices. Comparison of shear stress versus shear rate for flow behavior and viscosity versus shear rate for viscosity behavior were investigated. All emulsions exhibited shear thinning, pseudo plastic behavior over the entire shear rate. Formulated permanent label PSA had a lower yield stress point compared to unformulated latex, which shows easier processing capabilities for formulated CRE.

Oscillatory tests were investigated to further explore into the viscoelastic behavior of the PSAs. It was understood that permanent label emulsion CRE-L1 had a wider linear viscoelastic region

compared to CRE-L2. Yield point, storage modulus, G' and loss modulus, G'' for CRE-L1 PSA were higher than CRE-L2 PSA in the permanent label category. This may explain the higher cohesive strength and hence higher peel performance observed for CRE-L1 permanent label adhesive compared to CRE-L2. Complex viscosity η^* , which is a function of complex shear modulus, G^* for CRE-L1 was higher, which provides further testimony to this observation. This may be attributed to the formulation additives used in CRE-L1 to achieve desired peel strength characteristics. Lastly for clear label CRE-CL, the YP of LVE and the flow stress point are greater than VC-L2 establishing that formulated clear label CRE-CL PSA will be much more stable under high shear conditions. This further shows that stability can be enhanced by proper choice of stabilizing reagents in CRE-CL.

References

1. Association of International Metallizes, Coaters and Laminators, (www.aimcal.org)
<http://www.aimcal.org/member-news/articles/id/5838/new-awa-study-the-north-american-label-market.aspx>
2. Emulsion Polymerization and Latex Applications, C. D Anderson and E. S. Daniels, *Rapra Reviews Reports*, Volume 14, No. 4, 2003 ISBN: 9781859573815.
3. Tarwat F. Tadros, *Rheology of Dispersions, Principles and Applications*, 2010, Wiley-VCH Verlag & Co. KGaA, Boschstraße 12, 69469 Weinheim, Germany ISBN: 978-3-527-32003-5
4. H. Senff and W. Richtering “Rheology of a Temperature Sensitive Core–Shell Latex”, *Langmuir*, 1999, 15 (1), pp 102–106
5. Marcelo do Amarala, Alexandra Roosb, José M. Asuaa, Costantino Cretonb, “Assessing the effect of latex particle size and distribution on the rheological and adhesive properties of model waterborne acrylic pressure-sensitive adhesives films” *Journal of Colloid and Interface Science*, Volume 281, Issue 2, 2005, Pages 325–338
6. L.G. Torresa, R. Iturbea, M.J. Snowdenb, B.Z. Chowdhryb, S.A. Leharne, “Preparation of o/w emulsions stabilized by solid particles and their characterization by oscillatory rheology, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 302, Issues 1–3, 20 July 2007, Pages 439–448
7. T. G. Mezger, *Applied Rheology*, 2015, Anton Paar GmbH, Austria ISBN: 978-3-9504016-0-8
8. <https://www.osha.gov/dsg/hazcom/global.html>
9. The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) adopted by United Nations (UN), 2003 http://www.unece.org/trans/danger/publi/ghs/ghs_rev02/02files_e.html
10. Living building challenge declare compliance guidance, <https://living-future.org/declare/compliance-guidelines>
11. Handbook of sustainable polymers, Processing and Applications, Editors: V. J. Thakur and M. K. Thakur. 2016, CRC Press, Boca Raton, FL

Acknowledgment

I would like to thank Vinavil Americas/MAPEI Corporation for their help, encouragement and support in preparation of this manuscript.