

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Synthesis and properties of soap-free P(2-EHA-BA) emulsion for removable pressure sensitive adhesives

Cite this: DOI:
10.1039/x0xx00000x

Lei Zhang,^a Yingjie Cao,^{bc} Lei Wang,^a Lu Shao,^a and Yongping Bai^{*a}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Pressure sensitive adhesives (PSAs) are materials that can adhere strongly to solid surfaces under a light contact pressure for a short time. Soap-free emulsion polymerization of 2-ethylhexyl acrylate and n-butyl acrylate has been performed in the presence of a reactive emulsifier SR-10 to obtain high adhesion properties of PSAs. The particle size distribution was quite narrow with the average diameter of 137 nm. FT-IR spectrum showed that the C=C bonds contained in monomers disappeared through the reaction. The DSC result showed that all the monomers were well copolymerized. The 180 ° peel strength could reach 183.2 N/m when SR-10 was 2 wt % and the ratio of 2-EHA to BA was 4 to 1. The tack was 13 #. The shear holding time was more than 100 h. The removable PSA tapes produced from the resulting soap-free emulsion showed good adhesion properties and stabilities, which are suitable for practical applications.

Introduction

Pressure sensitive adhesives (PSAs) are nonmetallic materials used to bond other materials.¹ PSAs can form a bond at low or no applied pressure with no activation by a treatment with solvent or heat. They are aggressively and permanently tacky in dry, solvent-free form at room temperature. PSAs have a combination of liquid-like viscous and solid-like elastic properties. Thus they can flow and quickly wet the adherend, and have sufficient cohesive strength to leave no visible residue when disbonded from the adherend.² The essential performance of PSAs is usually evaluated by tack, peel strength and shear holding power. The tack measures the ability of PSAs to adhere quickly, peel strength characterized its ability to resist removal by peeling, and shear holding power represents its ability to hold in position when shear forces are applied. The properties of PSAs will depend upon the balance of tack, peel strength and shear holding power.³ PSAs have been widely used in many scientific and industrial applications over the past few decades. PSA products are virtually ubiquitous in workplaces and homes, such as are tapes, labels, band-aid, protective films, sign and marking films. They can also be used in many highly sophisticated applications, such as drug-delivery patches and assembling tools.⁴

Emulsion polymerization is the major industrial process for PSAs of waterborne polymeric dispersions.⁵⁻⁷ In particular, emphasis on environmental responsibility has increased the importance of this technique. The most common type of emulsion polymerization is an oil-in-water emulsion. Polymer particles are obtained from radical polymerization of monomer, emulsifier and initiator in a continuous phase of water. Emulsion polymers are environmentally friendly alternatives to solvent-based polymers.⁸ The emulsion PSAs can be used as a thin layer over PP, PET or PVC substrates. Acrylate emulsion PSAs have been widely researched due to their environmental

safety, optical clarity and low cost.⁹⁻¹¹ In general, a PSA acrylic monomer composition comprises primary monomers, modifying monomers and functional monomers. There are several acrylic monomers used for primary monomers of PSAs, such as 2-ethylhexyl acrylate (2-EHA), butyl acrylate (BA), isooctyl acrylate and ethyl acrylate (EA), because the glass transition temperature (T_g) of PSAs should be lower than room temperature. Different monomers were used for PSAs according to the requirements of different applications.¹²⁻¹⁷

Traditional emulsion polymerization is performed in the presence of an emulsifier.¹¹⁻¹⁴ The existence of emulsifier with low molecular weight and the migration of emulsifier to adhesive surface make adhesion properties worse, especially shear holding power. Generally, the shear holding time of PSAs prepared by traditional emulsion polymerization is less than 24 h.¹⁸ The emulsifier can also have detrimental effects on stabilities, which makes the emulsion PSAs unsuitable for practical applications. In order to avoid the disadvantages resulted from the emulsifiers used in traditional emulsion polymerization, soap-free emulsion polymerization with reactive emulsifiers is needed. Reactive emulsifiers can react with monomers and become a part of the polymers. It decreases the negative effects of traditional emulsifiers on the nature of the emulsion.¹⁹⁻²³ Reactive emulsifiers without nonyl phenol groups and alkyl phenol groups should be used, since the use of nonyl phenol ethoxylates and alkyl phenol ethoxylates is restricted in many countries for its environmental endocrine disruptors.²⁴⁻²⁷ Reactive emulsifier SR-10 can provide the micelles for radical reaction. It is a kind of anionic reaction emulsifier, which can polymerize easily with various monomers, since it has an allyl group as a polymerizable part. There is no free emulsifier left in the emulsion after polymerization. It can help develop highly-functional emulsions, which is beneficial to adhesion properties and stabilities. The critical micelle concentration (CMC) of SR-10 is 7.3×10^{-4} mol/L, which

indicates that preferable emulsify effect can be realized by using less dosage.²⁸

In this work, soap-free P(2-EHA-BA) emulsion with good stabilities has been synthesized. It requires 2 wt % of SR-10 to get the adhesion properties of PSA tapes, which is better than other amounts of SR-10. And the optimal ratio of 2-EHA to BA is 4 to 1. The PSA tapes produced from the resulting soap-free P(2-EHA-BA) emulsion can be removed many times. And there is no residue of PSAs on the adherend. The soap-free P(2-EHA-BA) emulsion exhibits excellent adhesion properties for various practical applications.

Experimental

Materials

The monomers of 2-ethylhexyl acrylate (2-EHA), n-butyl acrylate (BA) and acrylic acid (AA) were purchased from Wuxi Jiani Chemical Co., Ltd. SR-10 was obtained from Adeka (Shanghai) Co., Ltd. Sodium dodecyl sulphate (SDS) and alkylphenol ethoxylates (OP-10) were provided by Shanghai Jingxi Chemical Technology Co., Ltd. NaHCO₃ was purchased from Shanghai Hongguang Chemical Co., Ltd. Ammonium persulphate (APS), and CaCl₂ were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. These materials were used as received. Deionized water (DW) was used throughout the whole experiment.

Emulsion polymerization

Soap-free emulsion was synthesized in the presence of SR-10. The pre-emulsion was prepared with a stirring speed of 1200 RPM for 0.5 h using DW (30 g), SR-10, 2-EHA, BA and AA (0.55 g). The monomers were total 55 g. DW (25 g), APS (0.15 g) and NaHCO₃ (0.11 g) were added into the flask which was dipped in a heating batch at 82 °C and kept at the temperature constant for 10 min. The stirring speed was 150 RPM. And the polymerization was conducted by drop-wise addition of the pre-emulsion and the initiator solution into the system which lasted about 1 h. The initiator solution consisted of DW (5 g) and APS (0.1 g). Then, the flask was heated to 85 °C and maintained for 1 h for the fully polymerization.

Traditional emulsion was synthesized in the presence of SDS and OP-10, with a ratio of 2 to 1.

Characterizations of soap-free emulsion

Infrared spectra were recorded on FTIR spectrometer (Perkin Elmer Inc, USA). DSC test was carried out with a DSC 200 F3 (Netzsch, Germany) apparatus under a heating rate of 10 °C/min. Particle size was measured by Mastersizer 2000 (Malvern Instruments Ltd, UK). Viscosity was measured by rotational viscometer (Brookfield Engineering Laboratories Inc, USA) at 25 °C. Stabilities were tested under various conditions of calcium ions, dilution, mechanical stir, low-temperature resistance and storage. CaCl₂ solution was consisted of CaCl₂ (5 g) and DW (95 g).

Preparation of PSA tapes

Soap-free emulsion was coated directly onto 110 μm corona PP film. The tapes were dried in an oven at 90 °C for 2 min. The thickness of the tape after drying was 125 μm.

Characterization of PSAs

Tack properties

A 100 mm×100 mm PSA tape was cut down. Steel balls of different size were released from the top of an incline with an angle of 30 degree. The number of the biggest ball which stopped on it was recorded.

180 ° peel strength

A tape strip with a width of 25 mm was attached to the surface of a steel sheet for the test of 180 ° peel strength. A roller moves on the tape back and forth 3 times. After a dwelling time of 30 min, the 180 ° peel strength at a distance of 75mm was tested by a tensile machine with a drawing speed of 300 mm/min.

Shear holding power

A tape strip of 25 mm×70 mm was cut for the test of shear holding power, with a roller moving back and forth three times to make a good contact. 20mm was applied on one sheet, and the rest for another. The sample was clamped vertically with a 2 kg load after a dwelling time of 1 h. The time cost between the start of loading and the complete separation of the tape from steel sheet was recorded.

Results and discussion

Adhesion properties

Effect of emulsion types

Pre-emulsion prepared with SR-10 was stable, while pre-emulsion prepared with SDS and OP-10 had obvious stratifications after 2h's standing. The efficiency of polymerizable monomer SR-10 for emulsifying was much better than traditional emulsifiers in this study.

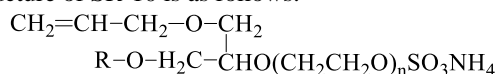
As Table 1 shows, the adhesion properties of PSA tapes prepared of soap-free emulsion are much better than those of traditional methods, especially the shear holding power.

Table 1 Properties of PSA tapes of different emulsion type

Emulsion type	Tack (#)	180 peel strength (N/m)	Holding time (h)
Traditional emulsion	7	92.4	6.6
Soap-free emulsion	13	107.6	46

Generally, traditional emulsifiers with low molecular weight are needed in normal polymerization method. The transfer of redundant emulsifier from the PSAs to adhesive surface causes slip phenomenon, which make the emulsion exhibit worse adhesive properties and stabilities. The holding time of soap-free emulsion is 46 h, which is much better than that of traditional emulsion of 6.6 h, which is because SR-10 was added in the soap-free emulsion.

The structure of SR-10 is as follows:



It is a kind of anionic reaction emulsifier, which can easily react with acrylate monomers and become a part of polymers without migration. Therefore, the adhesion properties of soap-free emulsion PSAs are much better than the other.

Effect of amounts of SR-10

Fig. 1 shows the PSA tapes has excellent tack properties. The tack increases from 12 # to 13 # when the amount of SR-10 increases from 1 wt % to 2 wt % and decreases at 4 wt %. And it is only 11 # with SR-10 of 5 wt % in monomers. With a small amount of SR-10, the cohesion of the PSAs tape is not enough. On the contrary, a large amount of SR-10 reduces the adhesion of the PSAs tape. It is difficult for steel ball to stop on the surface of PSAs tape. It can be observed that the PSA tapes has the higher tack properties when the amount of SR-10 is between 2 wt % to 3 wt %.

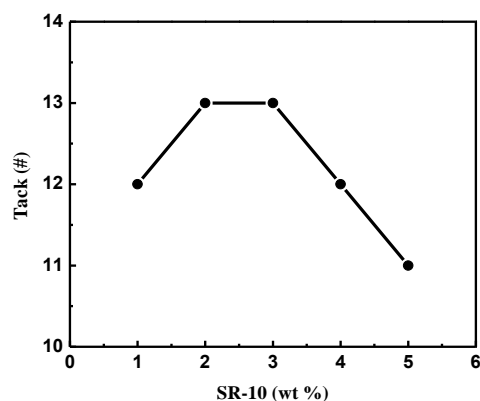


Fig. 1 Effect of SR-10 on tack properties of PSA tapes

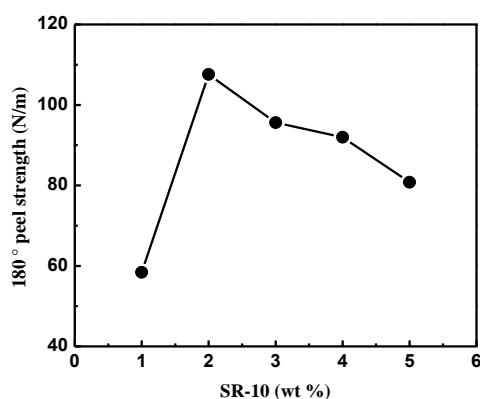


Fig. 2 Effect of SR-10 on 180° peel strength of PSA tapes

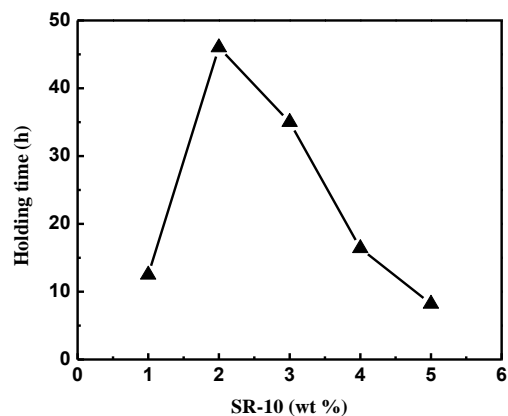


Fig. 3 Effect of SR-10 on shear holding power of PSA tapes

As shown in Fig. 2, the effect of SR-10 on the 180° peel strength of PSA tapes. The 180° peel strength increases when the amount of SR-10 increases. SR-10 can enhance the cohesive of polymer. The maximum value reaches 107.6 N/m with SR-10 of 2 wt % in monomers. After that, the 180° peel strength declines. SR-10 is reacted on the surface of particles. Too much SR-10 reduces the adhesive of PSAs.

Fig. 3 shows the effect of SR-10 on shear holding power of PSA tapes. As the amount of SR-10 increases, the holding time obviously increases from 12.5 h to 46 h. After that, the holding time declines. There are the less latex particles with the less amount of SR-10 whilst the particle size is relatively large. The surface wettability is low and the adhesive properties are weak. On the other hand, too much amount of SR-10 reduces the adhesion of the PSAs tape.

When the amount of SR-10 is less than 2 wt %, the micelles are easy to aggregate into larger particles, thus leading to the less latex particles. The strength of the adhesive layer is not strong enough, since it is not continuous enough in a very small scale with the moisture volatilization after coated on substrates. The surface wettability of the adhesive layer is low and the adhesive properties are weak. On the contrary, if there is too much SR-10 in the surface of adhesive layer after drying, the bonding force will be reduced between the polymer and the adherend. Hence, the properties of PSAs will decrease when the amount of SR-10 is more than 2 wt %. The optimal amount of SR-10 was 2 wt %.

Effect of amounts of BA

As is shown in Fig. 4, the PSA tapes have good tack properties. The tack is 13 # when the amount of BA is less than 20 wt %. After that, the tack properties decrease. BA has a higher T_g than 2-EHA, which can influence the tack properties of PSA tapes. The T_g of the polymer raised as well.

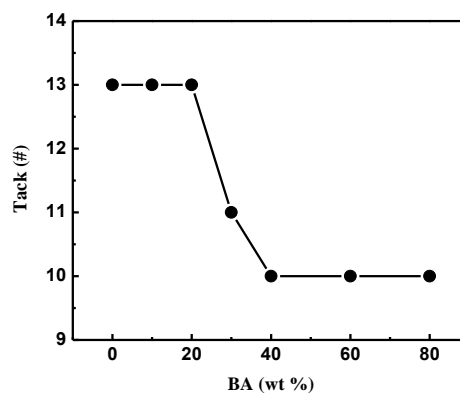


Fig. 4 Effect of BA on tack properties of PSA tapes

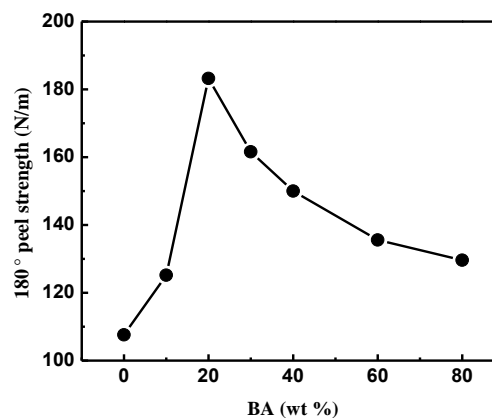


Fig. 5 Effect of BA on 180° peel strength of PSA tapes

The 180° peel strength of PSA tapes was also investigated as is shown in Fig. 5. The 180° peel strength increases with the growth of the amount of BA. The cohesion of polymer can be enhanced by BA. Furthermore, too much BA weakens the adhesion of the PSAs.

The properties of PSAs depend on the adhesion and cohesion. The 180° peel strength increases with the growth of the amount of BA. Sufficient cohesive strength is needed, in order to ensure that there is no damage to the adhesive layer when it is peeled off. The T_g of BA is higher than that of 2-EHA, which can enhance the cohesion of PSAs. However, too much BA will weaken the adhesion of PSAs. The 180° peel strength and tack properties decrease, when the brittleness is too high. Therefore, 20 % of using BA leads to the optimal performance.

Based on the above results, the optimal ratio of 2-EHA to BA is 4 to 1. The shear holding time is more than 100h. The soap-free P(2-EHA-BA) emulsion can primarily satisfy the requirement of shear holding power properties.

In this work, the PSA tapes produced from the resulting soap-free emulsion can be removed many times. The 180° peel strength is still more than 50 N/m after 1000 times of adhesion and removal. It is able to continue adhesion on the adherend. In this work, no traditional emulsifier with low molecular weight is used. SR-10 is copolymerized with monomers. Therefore, there is no PSAs residue on the adherend, which is suitable for removable PSAs applications.

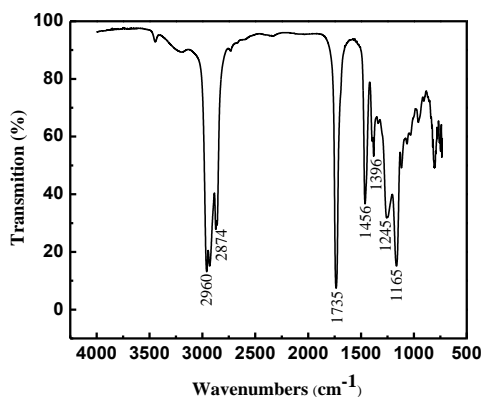


Fig. 6 FT-IR spectrum of P(2-EHA-BA)

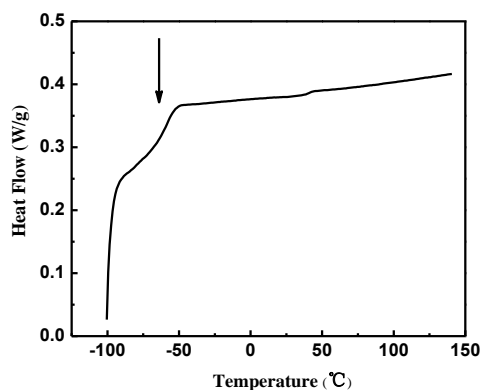


Fig. 7 DSC thermogram of P(2-EHA-BA)

Analysis of FT-IR

Fig. 6 shows the FT-IR spectrum of P(2-EHA-BA). 2960 cm^{-1} and 2874 cm^{-1} are attributed to the stretch vibration of $-\text{CH}_2$ and $-\text{CH}_3$. 1456 cm^{-1} and 1396 cm^{-1} suggest the bend vibration of C-H. The significant peaks at 1735 cm^{-1} and 1250~1000 cm^{-1} correspond to C=O and C-O group, respectively. The characteristic strong peak of C=C group near 1580~1650 cm^{-1} disappeared, which indicating C=C contained in monomers reacted already.

Analysis of DSC result

As is shown in Fig. 7, there is only one T_g of $-63.9\text{ }^\circ\text{C}$, which indicates that all the monomers were copolymerized. The T_g of PSAs is pretty suitable for practical applications.

Analysis of particle size

Fig. 8 shows the particle size distribution of soap-free P(2-EHA-BA) emulsion by volume, which is quite narrow. The average particle size is 137 nm. In this work, the monomers are dispersed sufficiently with a high stirring speed of 1200 RPM. Part of APS is added to the flask previously. During the drop-wise process, the drops can immediately react during the polymerization process since the polymerization system is in monomer-starved condition. The interaction between the EO segments of SR-10 with intermolecular hydrogen bonds can make electric double layers stable. From the results obtained so far, the PSA tapes have a good performance in adhesion properties.

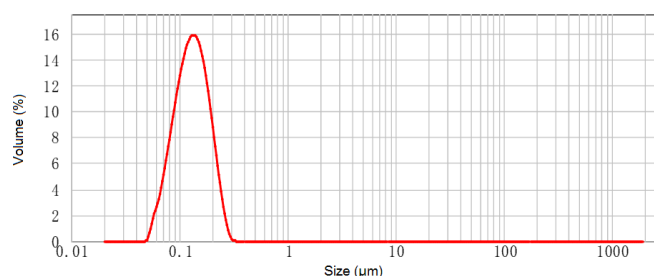


Fig. 8 Size distribution by volume of soap-free P(2-EHA-BA) emulsion

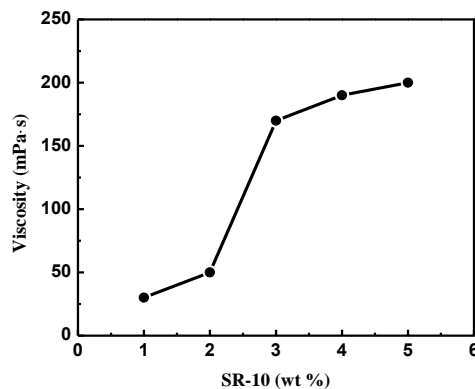


Fig. 9 Effect of SR-10 on viscosity of soap-free emulsion

Viscosity of soap-free emulsion

Viscosity of emulsion plays a primordial role on technique of sizing, since it affects the fluidity of emulsion. Marks will leave on the PP surface after coating, when the viscosity is too high. As shown in Fig. 9, the viscosity increases when the amount of SR-10 increases. A large amount of particles continuously generate with the sufficient emulsifiers in the system. When the amount of particles increases, the specific surface area increase as well, leading to a crowded population in limited area, thus the viscosity increases. The amount of SR-10 has a significant impact on viscosity. In this work, the viscosities of soap-free emulsions are all around 50 mPa s, when the amount of SR-10 is 2 wt %. It is suitable for coating directly on PP without adding any agent.

Stabilities of soap-free emulsion

Stabilities of soap-free emulsion were also tested under various conditions. The emulsion is mixed with 20 wt % of CaCl₂ solution for 48h, diluted to 3 wt % of solids content for 72h, stirred with a speed of 1500 RPM for 3h, placed at -5 °C in a freezer for 24 h, and keep properly at room temperature for 6 months. As a result, there are no obvious variations. The obtained results show that P(2-EHA-BA) prepared by soap-free polymerization has good stabilities.

In the process of soap-free polymerization, SR-10 provides negative charges on the surface of particles and forms stable electric double layers. At the same time, its volume effect prohibits the particles from getting close to each other as a spatial stability factor. Both effects enhance the stability of the particles. The requirements of stabilities for PSAs can be fulfilled.

Conclusions

Soap-free P(2-EHA-BA) emulsion for removable PSAs applications has been successfully synthesized. It is possible to obtain emulsion which has good stabilities with calcium ions, dilution, mechanical stirring, low-temperature resistance and storage. The PSA tapes produced from the resulting soap-free emulsion have fantastic adhesion properties, especially the shear holding power, which is more than 100 h. The tapes can be removed many times and there is no PSAs residue on the adherend, which has various promising practical applications.

Notes and references

^a School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, P.R. China. Fax: +86-451-86418270; Tel: +86-451-86413711; E-mail: baifengbai@hit.edu.cn

^b School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

^c Shanghai Zeafee Digital Inkjet Composite Material Co., Ltd, Shanghai 201605, P.R. China

- J. Sakdapipanich, N. Thananusont and N. Pukkate, *J. Appl. Polym. Sci.*, 2006, 100, 413-421.
- A. V. Pocius, in *Polymer Science: A Comprehensive Reference*, ed. K. Matyjaszewski and M. Möller, Elsevier, Amsterdam, Oxford, Waltham, 2012, Vol. 8, pp. 305-323.
- I. Benedek, *Pressure-Sensitive Adhesives and Applications*, Marcel Dekker, New York, 2004, ch.1, pp. 1-3.
- A. L. Li and K. C. Li, *RSC Adv.*, 2014, 4, 21521-21530.
- J. Kajtna, J. Golob and M. Krajnc, *Int. J. Adhes. Adhes.*, 2009, 29, 186-194.
- M. He, Q. Y. Zhang and J. Y. Guo, *Adv. Mater. Res.*, 2011, 8, 1785-1791.
- S. Roberge and M. A. Dubé *Polymer*, 2006, 47, 799-807.
- H. Lutz, H.-P. Weitzel and W. Huster, in *Polymer Science: A Comprehensive Reference*, ed. K. Matyjaszewski and M. Möller, Elsevier, Amsterdam, Oxford, Waltham, 2012, Vol. 10, pp. 479-518.
- G. E. Fonseca, T. F. McKenna and M. A. Dubé *Chem. Eng. Sci.*, 2010, 65, 2797-2810.
- N. Kohut-Svelko, R. Pirri, J. M. Asua and J. R. Leiza, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, 47, 2917-2927.
- L. L. Qie and M. A. Dubé *Int. J. Adhes. Adhes.*, 2010, 30, 654-664.
- M. R. Moghbeli, S. M. Zamir and B. Molaee, *J. Appl. Polym. Sci.*, 2008, 108, 606-613.
- H.Z. Shen, J.Y. Zhang, S.J. Liu, G.D. Liu, L.Q. Zhang and X.W. Qu, *J. Appl. Polym. Sci.*, 2008, 107, 1793-1802.
- A. Agirre, J. Nase, E. Degrandi, C. Creton and J. M. Asua, *Macromolecules*, 2010, 43, 8924-8932.
- C. Plessis, G. Arzamendi, M. Agnely, J. R. Leiza and J. M. Asua, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, 40, 2878-2883.
- A. Marçais, E. Papon, J. J. Villenave, P. Tordjeman, R. Pirri and P. Gerard, *Macromol. Symp.*, 2000, 151, 497-502.
- C. Plessis, G. Arzamendi, J. M. Alberdi, M. Agnely, J. R. Leiza and J. M. Asua, *Macromolecules*, 2001, 34, 6138-6143.
- L. Zhang, Y. J. Cao, S. Wang, Z. Crech, L. Shao and Y. P. Bai, *Int. J. Adhes. Adhes.*, 2013, 47, 69-72.
- K. Kang, C. Y. Kan, Y. Du and D. S. Liu, *J. Appl. Polym. Sci.*, 2004, 92, 433-438.
- K. Kang, C. Y. Kan, Y. Du and D. S. Liu, *Eur. Polym. J.*, 2005, 41, 439-445.
- T. T. Yang, H. Peng, S. Y. Cheng and J. P. In, *J. Appl. Polym. Sci.*, 2007, 104, 2438-2444.
- J. Wang, X. R. Zeng and H. Q. Li, *J. Coat. Technol. Res.*, 2010, 7, 469-476.
- F. A. Zhang, J. S. Kang and C. L. Yu, *J. Polym. Res.*, 2011, 18, 615-620.
- R. Höfer and K. Hinrichs, in *The Handbook of Environmental Chemistry*, ed. O. Hutzinger, Springer-Verlag, Berlin, Heidelberg, 2010, Vol. 12, pp. 97-145.
- A. M. Fernandez, U. Held, A. Willing and W. H. Breuer, New green surfactants for emulsion polymerization, *Prog. Org. Coat.*, 2005, 53, 246-255.
- R. Höfer and J. Bigorra, *Green Chem. Lett. Rev.*, 2008, 1, 79-91.
- C. Betton-Perez, Y. Z. Li and J. P. Ruiz, Proceedings of the Thirty Sixth Annual International Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, 2009.
- M. Hosaka, H. Shirai and N. Tsukuhare, *Paint and Coatings Industry*, 2013, 9, 72-78.