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Effect of 2-EHA as a soft monomer on the adhesion properties of PSAs synthesized by Emulsion Semi-Batch Terpolymerization Process Using Hybrid Emulsifiers

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Abstract

In order to obtain suitable formulation of designing direct synthesis of acrylic polymer emulsions to be used as EPSA, having high shear resistance together with high peel strength and tack, free radical emulsion polymerization of hard monomers, such as styrene (St), vinyl acetate (VAc), methyl methacrylate (MMA) and butyl methacrylate (BMA), and soft monomers, butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) along with multifunctional monomers, namely acrylic acid (AA), were carried out and an optimized composition of the acrylic monomers, 69 parts BA, 25 parts VAc, 5 parts BMA and 1 parts AA which are all in terms of the total weight of the monomers was obtained. For the investigation of the Effect of 2-EHA as a soft monomer on the adhesion properties of PSAs, the effect of varying the n-BA/2-EHA monomer composition on the adhesion performance of optimized PSA was investigated in terms of tack, peel and shear resistance, stability of emulsion latex, and its appearance. A decrease in the peel strength was observed although still having high peel strength when the 2-EHA content was increased to more than 50%. When the 2-EHA content increased to more than 50%wt, the peel strength was retained at a constant level.

Keywords: hard monomer, soft monomer, emulsion polymerization, hybrid emulsifier, 2-ethylhexyl acrylate, pressure sensitive adhesives.

Introduction

Pressure sensitive adhesives (PSAs) are viscoelastic materials that can adhere to solid surfaces in a short time with an aid of light pressure [1]. PSAs are widely used at the industrial scale as labels, tapes and protective films [2]. From the basic research point of view, the tack property of such adhesives is a very interesting behavior. Indeed, for the viscoelastic materials to have the property of tack, adhesion must be developed during the bonding step and cohesion during debonding step. To balance these conflicting properties, PSAs are generally based on complex formulations, including a polymer base that gives cohesion [2]. Nevertheless; there is another way of giving these properties to PSAs which is direct synthesis of them by polymerization processes. In this study, the Effect of 2-EHA as a soft monomer on the adhesion properties of PSAs is investigated.

Experimental

Material used

n-Butyl acrylate (n-BA) and 2-ethylhexyl acrylate (2-EHA) were purchased from BASF Chemical

Company. Methyl methacrylate (MMA), butyl methacrylate (BMA), styrene (St) and vinyl acetate (VAM) monomers all were purchased from Shazand Petrochemical Co (Arak, Iran) and were distilled in vacuum and stored at 0-5°C before use. Nonylphenol Ethoyleate (KENON 30) as nonionic emulsifier were purchased from Kimyagaran Emrooz Chemical Industries Co. Ammonium persulfate (APS, 99%; Aldrich, Lancaster, UK) was used as free radical initiator as supplied.

Synthesis of PSAs

PSAs were prepared as approximately 50% solid content latexes by semibatch polymerization. Water (40 phr) and ammonium persulfate (0.1 phr) as a polymerization initiator were fed to a 1 L glass reactor equipped with a stirrer, a temperature controller and a reflux condenser. The mixture was heated to 80 °C. There to was added 100 parts of the monomer mixture, 60 parts of water, 5 parts of KENON 30 as an emulsifier. The resulting mixture was stirred and emulsified to prepare a pre-emulsion. The total amount of pre-emulsion was continuously to the glass reactor with the speed 1.6 ml/min for the first hour and 0.71 ml/min for the next 3 hours while effecting emulsion polymerization with stirring in



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this period at 83 °C, after which stirring was continued at 85 °C for a further hour to complete the polymerization.

The effect of varying the n-BA/2-EHA monomer composition on the adhesion performance of PSAs was investigated in terms of tack, peel and shear resistance, stability of emulsion latex, and its appearance. Different ratios of n-BA/2-EHA, 1:0, 2:1, 1:2, and 0:1, were selected as soft monomers in the optimized formulation according to initiator concentration, content and type of hybrid emulsifier, and type and level of hard monomers in order to carry out semibatch emulsion polymerization, resulting in production of PSA33, PSA34 and PSA35. The results are shown in Table 1. Also, two commercial PSA samples, V205 and V218, which are two of the commonest industrial PSA, manufactured by BASF Company, were tested and their adhesion properties were reported and contrasted with PSA33, PSA34 and PSA35 in this table.

Results and Discussion

Regarding the results reported in Table 1, a decrease in the peel strength was observed although still having high peel strength when the 2-EHA content was increased to more than 50%. When the 2-EHA content increased to more than 50%wt, the peel strength was retained at a constant level. This behavior can be explained by the relation between viscoelastic dissipation energy produced during adhesive debonding and the molecular network parameters of the acrylic adhesives, M_c (crosslink molecular weight of the microgels) and M_e (the entanglement molecular weight of the free chains in the adhesive network morphology). According to the studies of Moghbeli and his coworkers, with an increase in the 2-EHA content in the adhesive composition, M_c showed a peak at 50%, whereas M_e increased uniformly. Nonetheless, the M_c/M_e decreased only as the 2-EHA level increased adhesive which showed that fracture energy during adhesive debonding was lowered as M_c/M_e decreased. In other words, by an increase in the 2-EHA level to 50 wt% and in increase in M_e , the bulk-fracture energy of acrylic PSAs was decreased. At higher M_c/M_e values, the microfibrils needed higher energy to deform and fracture during the peeling process. By an increase in the 2-EHA level above 50 wt%, no significant change in peel was observed although the M_c/M_e value of the PSAs decreased [3]. This behavior could be attributed to other parameters that affect the peel strength

according to the adhesion rheological model presented by Gent and Schults [4].

Interestingly, a synergistic effect in increasing the shear resistance was observed at 67wt% 2-EHA of the total soft monomer level. This behavior could be attributed to a good interconnection between the microgels and the free chains of the contacting particles in the PSA film. The EPSA with the ratio 67%/34% wt of 2-EHA/BA showed the highest shear resistance, 900kPa, in contrast with all other PSAs synthesized in this study and the commercial EPSA reported in Table1. Above the 67 wt% level of 2-EHA in the monomer feed, the shear resistance started to decrease. This behavior was in accordance with what was reported by Torbing et al, who showed that acrylic PSAs with $M_c > M_e$ and $M_w > 2M_e$ achieved a high shear resistance without a significant trade-off in peel and tack.

Table 1. The effect of 2-EHA on the final properties of PSAs

| Sample No | BA%/2-EHA% | %Solid | Tack (cm) | Shear (kPa) | Peel (N/mm) | T_g (DSC) |
|-----------|------------|--------|-----------|-------------|-------------|--------------------|
| PSA29 | 100 | 49 | 7.6 | 386 | 0.97 | -37 ⁰ c |
| PSA33 | 67/34 | 50 | 6.5 | 296 | 0.58 | -46 ⁰ c |
| PSA34 | 34/67 | 50 | 5.5 | 900 | 0.55 | -63 ⁰ c |
| PSA35 | 100 | 50 | 4.5 | 525 | 0.53 | -55 ⁰ c |
| PSA36 | - | - | 8 | 700 | 0.42 | - |
| PSA37 | - | - | 6 | 504 | 0.53 | - |

Conclusion

Effect of 2-EHA on the optimized tack properties of PSA was studied using different levels of hybrid of two soft monomers, 2-EHA/BA in the synthesis of acrylic terpolymer. A substantial increase in the shear strength was observed at 67 wt% 2-EHA in the monomer composition of soft monomers, 2-EHA/BA or 47 parts of 2-EHA in the total monomer composition, without a significant trade-off in peel strength and tack.

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