International Journal of Adhesion & Adhesives 55 (2014) 64–68

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

An oligomeric switch that rapidly decreases the peel strength of a pressure-sensitive adhesive

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ARTICLE INFO

Article history:
Accepted 28 June 2014
Available online 1 August 2014

Keywords:
Adhesive switch
Pressure-sensitive adhesive
Oligo(glycerol sebacate)
OGS
Peel force

ABSTRACT

The development of medical pressure-sensitive adhesives that possess high peel force when in contact with the skin and low peel force when removed from the skin is a noteworthy area of research. The means by which the peel force has been modulated in the past has included physical approaches (peel angle, deformation of skin, substrate material, etc.) and chemical processes that implement a "switch" that can be activated during removal to significantly reduce the peel force of the adhesive. Herein, we report the application of oligo(glycerol sebacate) (OGS) as an adhesive "switch" that is activated via the use of isopropyl alcohol (IPA) to promote a rapid decrease in peel force during removal of a medical pressure-sensitive adhesive. Furthermore the decrease in peel force is approximately 90%, and occurs on a clinically manageable time-scale (20 s). The technology found within this paper is amenable to current manufacturing processes and is ready to be implemented in medical pressure-sensitive adhesives so that healthcare providers, patients, and consumers might have a means of diminishing pain and trauma during the removal of bandages and/or medical dressings.

1. Introduction

Since the advent of pressure-sensitive tape in the mid-1800s [1] and the adhesive bandage in 1920 [2] a significant amount of research has been focused on developing bandages and medical dressings that enhance patient comfort and overall satisfaction. A study by Hollinworth and Collier concluded that dressing changes are in fact one of the most painful and traumatic wound care procedures [3]. The pain associated with dressing changes has been shown to be accompanied by a negative psychological aspect that contributes to a decline in patient comfort and leads to physiological stresses [4]. The pain and trauma associated with dressing removal has been intensely studied, and research shows that approximately 1.5 million cases of medical adhesive removal injuries occur each year in the U.S. alone [5,6]. These injuries span a broad spectrum that includes mild skin irritation to permanent scarring and decreased mobility. A major injury that frequently occurs is skin stripping and can result in pain, soreness, inflammatory processes, and an infection at the wound site depending on the severity and depth of skin removal [7–11]. Neonates and the elderly are two age groups particularly susceptible to skin stripping and injury due to the friable nature of their skin [12,13]. Therefore, these two demographics make up a considerable amount of the reported injuries related to the removal of adhesive dressings. Furthermore, if a significant intervention in wound care treatment is not realized soon, the number of these types of injuries will only increase as the number of people over 60 is projected to increase 3.5 times faster than the total population increase by 2025 [14].

Various factors contribute to the type of injury one receives from the removal of an adhesive dressing, which include age of individual, moisture level of skin, wound site, frequency of dressing change, and adhesive strength [15]. From these various factors, the patient's age and the adhesive strength are probably the most important when considering the potential injury that might be sustained by the patient. Unfortunately, out of these factors only adhesive strength can be modified or altered to minimize the pain and trauma associated with dressing removal. Hence, one must consider the trade-off to be made if the adhesive strength is to be altered [16]. To clarify, if a medical dressing is to be made with an adhesive that possesses low tack and peel strength then there is a possibility that the wound will be susceptible to bacteria and infection from an inadequate barrier around that wound. On the other hand, if the medical dressing is made with an adhesive that possesses high tack and peel strength

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http://dx.doi.org/10.1016/j.ijadhadh.2014.07.016
0143-7496/

so that the wound is securely protected from the environment then the risk for infection is diminished. However, if patient comfort is to be considered with these two examples (i.e. pain and trauma during dressing removal), the former situation would impart a high level of comfort during removal due to the low adhesion between the dressing and skin, while the latter situation would be painful and offer minimal comfort to the patient. Therefore the holy grail of bandages and medical dressings would be one in which its application gave an immediate strong bond to the skin, and then removed at will without any effort or pain.

Efforts to reduce the pain and trauma associated with dressing changes while maintaining a sterile wound environment have been accomplished to some extent with the development of silicones [8,13], drug-loaded dressings [17], bio-inspired technologies [5,18,19] and specialty tapes [20]. While these "painless" technologies are a significant improvement over present dressings, they are likely difficult to translate into clinical benefits because of the complex nature of their manufacture and/or concomitant high cost. Here we report a new, low-cost technology that results in adhesive bandages and dressings with high tack while allowing the consumer to remove the devices "on-command" via the application of a releasing agent without leaving residue on the skin. Of significance is the ability to easily incorporate this technology into current manufacturing processes, which positively affects the cost to manufacture the desired medical dressings.

Oligo(glycerol sebacate) (OGS) is the pre-polymer of the biodegradable elastomer poly(glycerol sebacate) (PGS) [21,22] which is a thermally cross-linked polymer that has been utilized extensively in various biomedical applications. Some of these applications include soft-tissue replacement and tissue engineering [23–25], drug delivery systems [26], cartilage tissue engineering [27] and bone regeneration [28]. In contrast, OGS is not cross-linked and it can be dissolved in various solvents and melted below 100 °C.

2. Methods

2.1. Materials

Glycerol and sebacic acid were purchased from Sigma-Aldrich and medical grade acrylic adhesive was supplied by Henkel AG & Co. Monomers were utilized as supplied without any further purification. Polymerization of glycerol and sebacic acid was performed as previously described [29]. The resulting melting point of oligo(glycerol sebacate) OGS was measured using a Perkin-Elmer DSC 8500 and is 36 ± 1 °C.

2.2. Manufacturing process

The commercial coating facility dissolved OGS in ethyl acetate and then blended this solution with a Henkel high-tack acrylic (Duro-Tak 380-3954). The solvent-based adhesive mixture was transfer-coated onto a silicone liner and then laminated to a 3 mil matte polyethylene (PE) film, at a coat weight of 31 g/m^2. The coated film was perforated with a density of 46,500 holes/m^2 at 600 μm hole size. The coated and perforated rolls of film were sent to a commercial converting facility where they were converted to the desired products, packaged, and sterilized utilizing standard ethylene oxide sterilization methods. The samples were subjected to and passed ISO 10993-10:2010 and ISO 10993-5:2009 standard biocompatibility studies [30].

2.3. Peel strength

To obtain peel strengths, a Labthink® PARAM® BLD-200N auto-stripping tester was utilized with adhesion to stainless steel plates. The experiments were performed according to a modified ASTM-D3330 [31] method at 25 °C and 40% RH. Each 2 in. × 1 in. sample was adhered to the stainless steel plate by passing a 2 kg roller over the sample 5 times. The samples were tested within 1 min of application to the stainless steel plate. The samples were peeled from the stainless steel plate at a rate of 300 mm/min and a peel angle of 180°. To probe the switching property of the adhesive, isopropyl alcohol (IPA) was applied to the PE backing of the adhered samples using a spray bottle that was positioned 3 in. away from the sample at an angle of 45°. Next, the samples were removed at discreet time intervals. Note: there is a 5 s initiation of the auto-stripping tester that does not record the peel strength as the sample is removed from the plate. Therefore, the peel strength at 20 s would actually be recorded at 15 s on the graph. The adhesive samples were tested with and without the use of IPA to demonstrate the decrease in peel strength as a function of IPA application and time. Each experiment was performed 10 times to ensure a competent sample size.

3. Results and discussion

3.1. Performance of IPA-induced switchable adhesive

To determine the efficacy of this technology and its viability in the commercial marketplace, there are various factors that need to be investigated such as the time-dependence of IPA penetration, concentration of IPA, the perforation density of the film, and the size of the perforations in the film. The effects of these factors are very important as a healthcare provider or consumer would be unwilling to wait an inordinate amount of time before removing a medical dressing, and if these dressings are to be perforated then the amount and size of perforations must be optimized to ensure a high level of adhesion while in use and ease of removal during dressing changes. The present investigation is concerned with the time-dependence of IPA penetration and the effect of IPA concentration.

The time-dependence of IPA penetration and its relationship to an observable decrease in peel strength were investigated to determine the amount of time required to afford the maximum drop in peel strength (Fig. 1).

From Fig. 1 one can observe that the pressure-sensitive adhesive possesses a high level of adhesion, which is demonstrated by

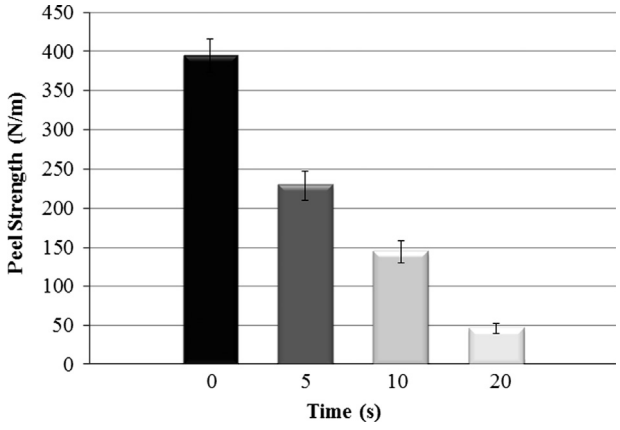

Fig. 1. Reduction in peel strength as a function of time after application of 91% IPA to a 3 mil PE film coated with 20% OGS/80% acrylic.

the peel strength value of 395 ± 21 N/m when no IPA is applied. Application of 91% IPA to PSA-coated 3 mil matte PE films was shown to affect the peel strengths for all time-dependence experiments. After 5 s there was an approximate 50% decrease (229 ± 19 N/m) in the peel strength of the adhesive film that steadily decreased with time until a maximum drop in peel strength of approximately 90% (46 ± 7 N/m) was observed at 20 s. Furthermore, if the experiment was allowed to extend beyond the 20 s, there was no further decrease in peel strength (data not shown). Since it was determined that 20 s was the amount of time required to afford the maximum drop in peel strength, the effect of IPA concentration was then investigated while holding time constant (Fig. 2).

Once again the maximum peel strength of the adhesive is 395 ± 21 N/m, which is dramatically reduced after applying IPA to the adhesive test strip and waiting 20 s. The significance of this statement can be evidenced by the peel strength values for both the 91% and 70% IPA experiments, which are 46 ± 7 N/m and 46 ± 5 N/m, respectively. Although there was a decrease in the peel strength for the 35% IPA experiment it was not as significant (138 ± 43 N/m) as the peel strengths for the other IPA concentrations, and the spread of values obtained within this experiment was much larger than the spread of values observed for the 91% and 70% IPA experiments. Although the 35% IPA experiment did not produce the significant reduction in peel strength observed during the 91% and 70% IPA experiments, it did produce an approximate 50% decrease in peel strength which could still be useful in clinical applications.

There is a perceived notion that IPA will cause healthy, unbroken skin to become dry and eventually compromised. However, there has never been any research to confirm this hypothesis. On the contrary a paper by John M. Boyce, MD, stated, "This concept has also been shown not to be true [32]." In an effort to demonstrate that the acrylic and OGS mixture is not merely dissolved upon contact with IPA, but that it reversibly swells to promote the observed decrease in peel strength a study was performed to probe the recovery of adhesion after IPA application and subsequent evaporation. In this study, IPA was applied to a sample strip that was adhered to a stainless steel plate and peel testing was initiated after discreet time intervals (Fig. 3).

From the results in Fig. 3, it was confirmed that without the application of IPA to the sample test strip (control) the maximum peel strength of the coated PE film was 398 ± 11 N/m. Upon application of IPA to the test strip and immediate initiation of the peel tester, it was observed that the peel strength was diminished by approximately 50% (213 ± 19 N/m). The magnitude of the observed decrease in peel strength is similar to what is

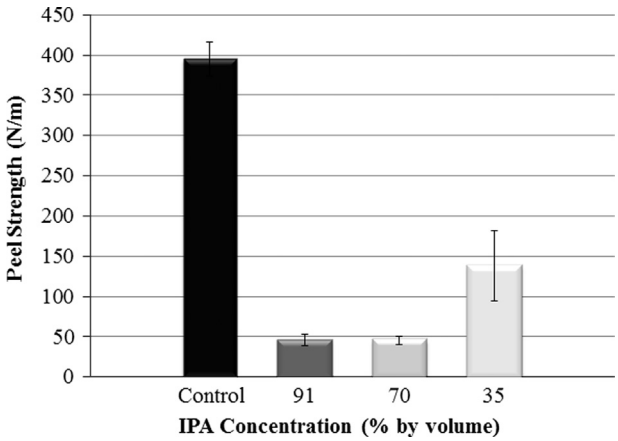

Fig. 2. Reduction in peel strength as a function of IPA concentration while holding time constant at 20 s.

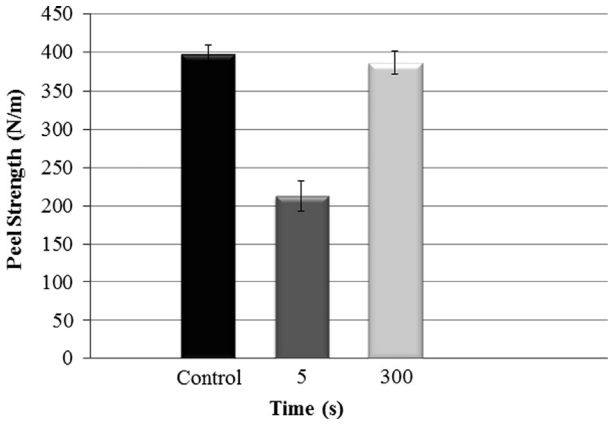

Fig. 3. Recovery of peel strength demonstrated after evaporation of 91% IPA.

observed during the time-dependence experiments (vide supra). To probe whether the peel strength might fully recover once IPA has evaporated from the film, IPA was applied to the test strips in a similar manner as noted above but in this experiment 5 min was allowed to elapse before peel testing was initiated. From the data in Fig. 4, it is evident that the peel strength of the coated PE film does in fact recover to its maximum level (386 ± 15 N/m).

To probe the mechanism of adhesive recovery, 2 in. × 1 in. sample films were adhered to a steel plate and its total mass was obtained. Next, the appropriate amount of IPA was applied to the sample film and the mass was once again obtained. Finally, the IPA was allowed to evaporate over a period of 5 min at which point the mass of the sample film and steel plate was once again obtained. This experiment was performed 10 times to ensure a competent sample size. Interestingly, 83.5 ± 5.2% of the IPA applied to the sample film evaporated within 5 min. Furthermore, this finding is in good agreement with the recovery data that was obtained (Fig. 3).

To investigate whether the acrylic OGS mixture was dissolved by IPA, and subsequently promoted the decrease in peel strength, the amount of residue that remained on a steel plate after a peel test was investigated. First, a clean, dry steel plate was weighed to obtain its mass. Next, a 2 in. × 1 in. sample film was adhered to the steel plate and the entire fixture was placed into the auto-stripping tester and subjected to a peel test experiment. An appropriate amount of IPA was applied to the film and the peel tester was initiated after 15 s to obtain the maximum decrease in peel strength. Once the film had been peeled from the steel plate the plate was removed from the auto-stripping tester and set aside for 5 min so that most of the IPA had evaporated. The steel plate was re-weighed to determine if the IPA had dissolved the adhesive mixture and left a residue on the steel plate. Interestingly, the increase in mass associated with the residue (0.0002 ± 0.0006 g) was identical to the experimental error based on the control experiment (0.0002 ± 0.0006 g). Therefore, it is reasonable to conclude that IPA removes an insignificant amount of adhesive from the film. The implications of these findings are multifaceted in that the acrylic and OGS mixture is not dissolved by the IPA to reduce the peel strength of the coated PE film; there is no residue after peeling the tapes, and the films can be applied to the indicated region, gently removed via IPA application, and then reapplied if necessary, and IPA is an excellent switching agent for this technology.

It would be very useful to know the minimum amount of IPA needed to trigger the release of the adhesive. However, due to the high vapor pressure of IPA, it was not possible to reliably measure this minimum amount. Therefore, the upper limit for the amount of IPA utilized was obtained. This was accomplished by measuring

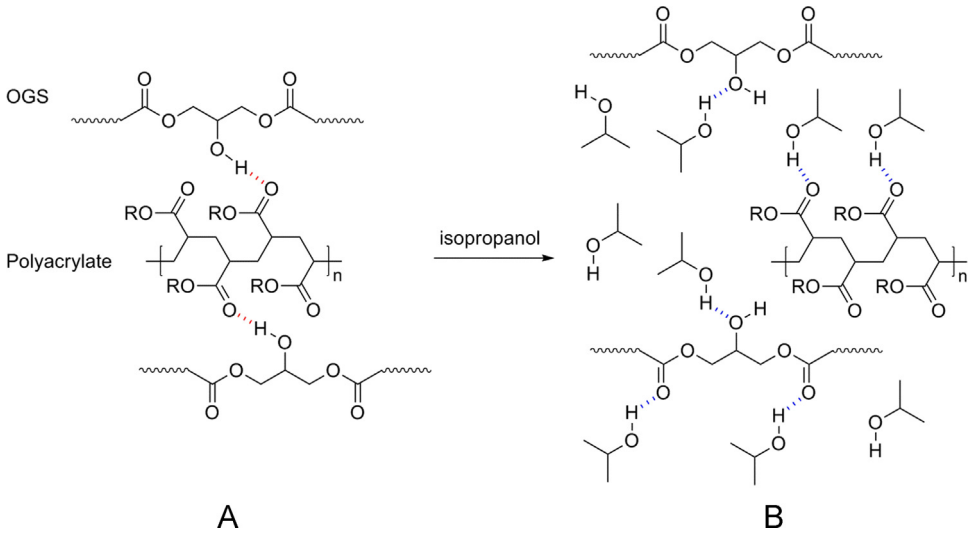

Fig. 4. (A) Representation of the hydrogen bonding that occurs within OGS and polyacrylate mixture. (B) After application of IPA the hydrogen bonding sites are disrupted via IPA exchange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the mass of a spray bottle filled with IPA, spraying the bottle twice to dispense the desired amount of IPA, and then measuring the mass of the spray bottle again to determine the total mass of IPA applied. The upper limit for the amount of IPA applied to each 2 in. × 1 in. sample was determined to be 0.311 ± 0.005 g. This set of experiments was performed 10 times to obtain a competent sample size. Although the amount of IPA required in the above experiments was a function of sample size, it is also related to perforation density. Therefore, it is expected that as the perforation density of the film is increased, the amount of IPA and time required to observe a similar decrease in peel strength would decrease accordingly. It should be noted that this upper limit significantly overestimated the amount of IPA that contacted the tape since over half of the sprayed IPA was lost in air and did not land on the tape.

3.2. Statistical analysis

Statistical differences for the time-dependent and concentration-dependent studies were determined using analysis of variance (ANOVA). Statistical differences were considered significant when $p < 0.05$. The sample size of each group was $N = 10$. With regard to the time-dependent study it was determined that $p < 0.001$, and *F*-Statistics was 819.2 which was significantly larger than the *F*-Table value of 2.9. Therefore, it can be concluded that at the 5% significance level the means for the time-dependent study are not equal. With regard to the concentration-dependent study it was determined that $p = 0.000$, and *F*-Statistics was 43.18 which was larger than the *F*-Table value of 3.35.Therefore, it can be concluded that at the 5% significance level the means for the concentration-dependent study are not equal. An independent-samples *t*-test was utilized for the recovery of peel strength studies. A statistically significant difference was not found when the control and 300 s samples were compared ($t(18) = 2.01$, $p = 0.059$; Control $M = 0.398$, 300 s $M = 0.386$). A statistically significant difference was found when the 5 s and 300 s samples were compared ($t(18) = 22.2$, $p = 0.0001$; 5 s $M = 0.213$, 300 s $M = 0.386$).

3.3. Mechanism of action

The hypothesized mode of action for release of the PSA-coated films upon application of IPA is thought to occur by disruption of intermolecular forces, and is graphically represented in Fig. 4.

Specifically there are multiple sites of hydrogen bonding that bolster the cohesiveness of OGS, and these same hydrogen bonding sites interact with the acrylic adhesive that is bonded to the substrate (skin) (Fig. 4A, red dashed lines). When IPA is applied to the adhesive, OGS swells via absorption of the IPA which disrupts the hydrogen bonding that occurs between acrylic, OGS, and the skin through IPA exchange (Fig. 4B, blue dashed lines) and the adhesive "releases" from the skin. Since OGS swells in IPA before dissolution, it is possible that the physical action of swelling of OGS contributes to the decrease in adhesion as well.

4. Conclusion

A novel adhesive formulation has been developed that allows the bonding and the debonding processes to be decoupled. This is evidenced by the high peel strength of the adhesive before IPA application, which is significantly reduced by approximately 90% after the application of IPA. A noteworthy characteristic of this adhesive formulation is that the maximum reduction in peel strength is achieved within 20 s after IPA application, which is a realistic amount of time when utilized in a clinical setting. Although compromised skin may be irritated by IPA the present formulation easily controls the region of skin that IPA contacts, thereby eliminating exposure of damaged skin to IPA. In addition, non-perforated adhesive dressings can be removed by applying IPA directly at the skin–adhesive interface. A very appealing aspect of OGS is that it can be incorporated into current adhesive coating processes with minimal changes to existing manufacturing processes. Finally, 70% IPA is readily available at low cost over-the-counter and requires no alteration to function as the triggering agent.

Acknowledgments

The authors are grateful to Jin Gao for thoughtful input during initial discussions.

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