J Nanopart Res (2011) 13:1029–1037
DOI 10.1007/s11051-010-0091-3

RESEARCH PAPER

# Characterization of English ivy (*Hedera helix*) adhesion force and imaging using atomic force microscopy

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Received: 20 January 2010 / Accepted: 14 September 2010 / Published online: 30 September 2010


**Abstract** English ivy (*Hedera helix*) is well known for its ability to climb onto and strongly adhere to a variety of solid substrates. It has been discovered that the ivy aerial rootlet secretes an adhesive composed of polysaccharide and spherical nanoparticles. This study aims to characterize the mechanical properties of the nanocomposite adhesive using atomic force microscopy (AFM). The adhesive was first imaged by AFM to visualize the nanocomposite. Mechanical properties were then determined at various time points, from secretion to hardening. The experimental results indicate that the ivy adhesive exhibited strong adhesion strength and high elasticity. There was a decrease in adhesive force over time, from 298 to 202 nN during the 24-h study. Accompanying with it were the limited changes in extension length and Young's modulus. The limited curing process of the ivy adhesive helps fill gaps in the attaching surface, leading to more intimate contact and increased van der Waals interactions with the surface. However, study based on a mechanical model indicated that van der Waals force alone is not significant enough to account for all of the measured force. Other chemical interactions and cross linking likely contribute to the strong adhesion strength of ivy.

**Keywords** Ivy · Nanoparticle · Adhesion force · Atomic force microscopy · Nanobiotechnology

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## Introduction

*Hedera*, or ivy, is a genus containing approximately 16 species of climbing or ground-creeping evergreen plants (Jennifer and Jun 2003). On suitable surfaces, such as trees and rock faces, ivy has the ability to climb 25–30 m above the ground and hold fast to vertical surfaces. This unique ability to climb has drawn great interest from scientists as early as the 1800s. Charles Darwin first observed that the aerial rootlets produced on creeping and climbing stems "secreted *a little yellowish matter*" upon first contact with an attaching surface (Darwin 1876). Little progress has been made in determining the structure and composition of this yellowish adhesive since the initial observation from Darwin. In the mid 1970s, Endress and Thomson investigated the adhesive of Boston ivy (*Parthenocissus tricuspidata*), using transmission electron microscopy (TEM) (Endress and Thomson 1976, 1977). Their studies provided

in-depth details about the structure of attaching Boston ivy tendrils, but limited information about the nature of the secreted adhesive. Other studies have focused on the morphology of the rootlets using light and scanning electron microscopy, but have not provided information on the structure and composition of the adhesive (Moens 1956; Melzer et al. 2010). In 2008, Zhang et al. conducted one of the first studies focused on identifying the structural components of the adhesive secreted from naturally growing ivy rootlets. Using atomic force microscopy (AFM), they observed a high abundance of uniform nanoparticles deposited onto the attaching surface. These nanoparticles were about 70 nm in diameter, and were observed on a variety of surfaces including mica, silicon wafer, and glass (Zhang et al. 2008). From the discovery, it is hypothesized that nanoparticles are the key component that generates the strong adhesion used by ivy to climb vertical surfaces.

Intense research has been conducted over the last decade on the contribution of nanostructures to surface adhesion. One of the most celebrated examples is the discovery of nanofibers on the gecko footpads. The existence of these abundant and deformable nanofibers maximizes the intimate contact area between the toes of the gecko and the climbing surfaces. This intimate contact facilitates inter-molecular interactions through van der Waals force (Autumn et al. 2002; Peattie and Full 2007). Similar attachment mechanisms have been observed in flies, beetles, and lizards (Steinbrecher et al. 2010). Although these studies have focused exclusively on dry adhesion and on fibrillar structures from the micro- to nano-scale, shape-insensitive optimal adhesion has been studied in mathematic models (Gao and Yao 2004). From these models, it was predicted that for nano-sized structures, shape is not as important as the size of the structure in relation to generating adhesive strength. Following this principle, we expect that nanoparticles offer the same potential for surface adhesion due to their size scale.

A theoretical model was recently developed by our group to evaluate the impact of van der Waals interactions between ivy nanoparticles and solid substrates. From the model, it was confirmed that van der Waals force alone was significant to account for the strength of attachment of ivy (Wu et al. 2010). Experimentally, various nanoparticles have been tested to enhance adhesive strength or as filler for polymeric adhesives (Zhai et al. 2006; Corkery et al. 2008). Although it is not clear whether the nanoparticles contribute directly or indirectly to the strength of adhesion, a recent study has provided firm evidence of the adhesion ability of polystyrene nanoparticles (Xing et al. 2010).

The existence of adhesive nanoparticles will prompt their potential applications in a variety of fields. Nanoparticles have already been explored as fillers in the glue industry. Adherent nanoparticles also hold a significant promise to future research in drug delivery. Biodegradable nanoparticles provide controllable, sustained drug delivery in vitro (Panyam and Labhasetwar 2003). In vivo studies, however, have shown that nanoparticles are not effective at adhering to vascular walls under shear stress. Adherent nanoparticles may overcome this deficiency, allowing the lingering of nanoparticles in activated or inflammatory endothelial cells under fluid shear stress thus improving the cell uptake of drug-carrying nanoparticles. An additional advantage of ivy nanoparticles is their natural origin and biocompatibility which provide them extra potential use in medical and bioengineering fields. Ivy nanoparticles have recently been proposed to be a prospective candidate to replace metal-based nanoparticles for sunscreens (Xia et al. 2010). Biocompatibility combined with strong adhesion ability will make ivy nanoparticles an ideal active component in the design of bioglue, surgical suture, or other wound healing materials.

Before taking significant steps in the direction of proposed applications, it is essential to first understand the strength of the adhesive, as well as the principles involved in generating the attachment strength. In an effort to understand how nanoparticles contribute to the attachment strength, accurate measurement of the adhesive force at the proper scale was necessary. AFM is a fundamental tool used to determine nano-scale forces, and is accurate even when measuring intermolecular forces in piconewtons (Aoki et al. 1997). AFM can also be used to monitor the fundamental mechanical properties of materials such as adhesive strength, compressibility, and elasticity (Binnig et al. 1986; Muller and Dufrene 2008; Noy 2006; Xing et al. 2010). Small non-covalent interactions, such as van der Waals force, hydrophobic and electrostatic interactions, and protein folding can also be determined using AFM (Matthias et al. 1997; Châtellier et al. 1998). As such,

we have applied this AFM-based approach to examine the nano-scale material properties of the nanocomposite adhesive secreted from English ivy.

In this study, a method was first developed for growing English ivy rootlets in tissue culture, to eliminate concern over contamination and to control the growth stages of ivy rootlets. The adhesive of tissue-cultured rootlets was then compared to naturally grown rootlets for their nanostructures. Both were found to contain nanoparticles with similar shape and size. After confirming the existence of nanocomposite adhesive, its strength was further determined using force versus distance curves generated by AFM during the 24-h study. At the same time, the elasticity and extension length of the secreted adhesive were monitored, to collect useful data for analyzing and understanding the adhesive hardening process.

## Materials and methods:

### Sample preparation

Juvenile *Hedera helix* shoots, cut from a natural source on the University of Tennessee, Knoxville campus, were grown in a greenhouse under controlled temperature, humidity, and light availability. Leaves were removed from the shoots, and shoots were trimmed to 6 cm. Shoots were then sterilized using 1.23% sodium hypochlorite [20% (v/v) commercial bleach] plus 0.05% Tween 20, shaken at 200 rpm for 20 min, and subsequently washed with sterile water three times. Sterile shoots were then placed upright into Magenta GA7 boxes containing MS medium when they were grown at 24 °C at 16:8-h photoperiod under 82 μmol/$m^2$/$s^1$ irradiance (Murashige and Skoog 1962). Aerial roots were produced after ca. 2 days and were allowed to grow for an additional 2 days in MS media. Aerial roots were excised from source plants when they were approximately 3 cm in length. These were transferred to Petri dishes containing MS medium until analysis was performed (between 3 days and 2 weeks). In preparation for adhesive analysis, the tip of rootlets was gently cut under a bio-safety cabinet and touched on the silicon wafer surface to release the content. Samples were then either processed immediately, or allowed to air-dry in a bio-safety cabinet for at least 5 h.

### AFM imaging

The freshly prepared or air-dried ivy adhesive samples were scanned for the existence of nanoparticles using an Agilent 5500 AFM system (Agilent Technologies, Santa Clara, CA). The samples were imaged at room temperature (20 °C) using Picoview™ in AC mode, which minimizes sample distortion due to mechanical interactions between the AFM tip and the surface. To further optimize imaging, both the integral and proportional gains were adjusted to avoid excessive loading force applied to the samples. Using this system, three-dimensional imaging of the surface morphology with very high lateral and vertical resolution could be obtained. The probes used were commercially available silicon probes TAP300Al® (Budget Sensors, Sofia, Bulgaria) with a spring constant of 20–75 N/m, a resonant frequency of 300 ± 100 kHz, and a radius of curvature of less than 10 nm.

### Adhesive force measurement

To measure the adhesive properties of the ivy secretion, force versus distance curves were generated using an Agilent 5500 AFM system. The AFM probe was first calibrated with bare silicon wafer as a substrate to obtain a deflection sensitivity of 33.5 nm/V and a force constant of 4.33 N/m for the TAP150Al-G® (Budget Sensors) cantilever probes. The location of the adhesive was verified with a CCD camera mounted to a 10X objective, and the cantilever was moved over the center of the adhesive. Once the location had been established, approach of the tip was initiated and the tip was allowed to contact the sample surface for 2 s so that the probe and adhesive formed a complex. The tip was then withdrawn from the adhesive, and the deflection of the cantilever was measured. A series of 30 force curves exhibiting adhesion events were taken for each time point during the curing process. The mean and standard deviations were calculated using Microsoft Excel®. To calculate Young's modulus, the slope of the approach line for each force curve was obtained using Picoimage™ and was then applied to equation $E = (F/\mathrm{d}L)^*(L/A)$. In this equation, $E$ is the Young's modulus, $F/\mathrm{d}L$ is the slope of the approaching curve, $L$ is height of

the material, and $A$ is the contact area. The height of the material, $L$, was determined by imaging the adhesive and obtaining a vertical profile from the topography scan in Picoimage™. The area of contact, $A$, was calculated based on the diameter of the tip according to the manufacturer's specifications.

## Results and discussion

### Nanoparticles produced from in vitro ivy rootlets

Because of instrument limitation, a real-time monitoring of the attachment process of ivy at nano-scale in the fields becomes difficult. Also, concerns emerge for the contamination of environmental nanoparticles in the open air and for the growth stage difference of ivy rootlets in natural conditions. Thus, a method was first developed to grow English ivy rootlets in vitro. This method allowed us to have an opportunity to investigate the adhesives properties in different stages. For topographical characterization of the adhesives from cultured ivy rootlets, the rootlets were washed with 20-nm-filtered water and cut at the tips to release adhesive. Freshly prepared samples were extremely soft and prone to smearing by the AFM tip during the scanning. After 5 h of settlement, however, the adhesive could be clearly imaged. As shown in Fig. 1, the nanocomposite was mainly composed of nanoparticles 60–85 nm in diameter. The average diameter for the nanoparticles was 70 ± 6.5 nm, which was comparable to the previous report (Zhang et al. 2008).

This observation confirmed the previous report of nanoparticles in ivy adhesive. Nanoparticles embedded in a polymeric matrix are not unique to ivy adhesive. The existence of similar types of nanocomposites has been confirmed in the secretions of a variety of marine species, including polychaetes, mussels, barnacles, and sea stars (Stevens et al. 2007; Zhang et al. 2009; Berglin and Gatenholm 2003). The size of spherical particles in these adhesives is in the same range as those found in the ivy secretions, 60 nm for mussel, 80 nm for barnacles, and 50–100 nm for polychaetes and sea stars (Hennebert et al. 2008). The fact that these nanoparticles can be observed in a variety of species indicates a conserved approach to generating adhesive materials.

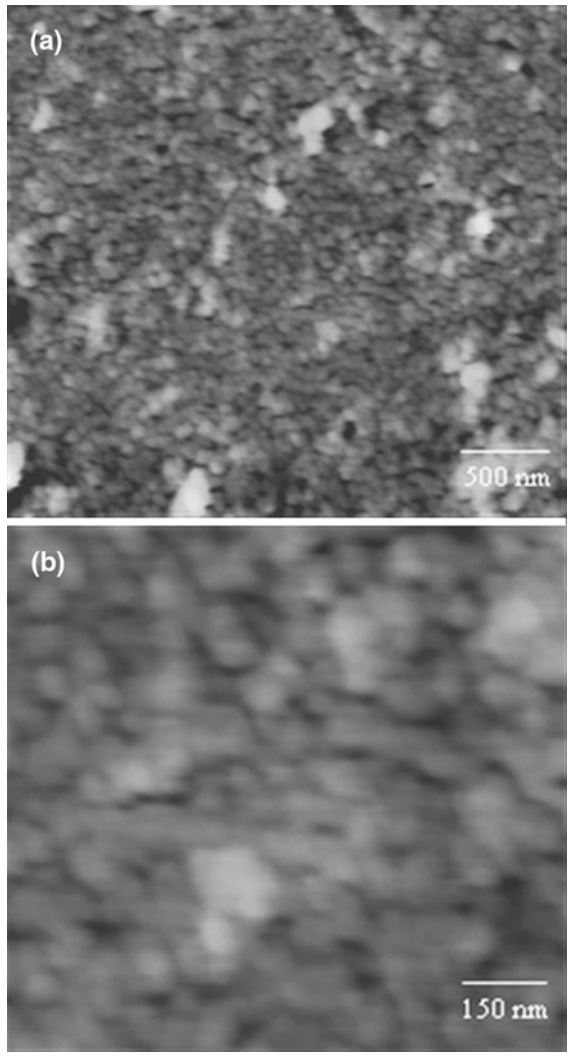


**Fig. 1** Nanoparticles released from the tip of in vitro grown ivy rootlets. AFM tapping-mode images of content from the tips of cultured ivy rootlets after 5 h of settlement. **a** 3.3 × 3.3 nm scanning window. **b** 1.0 × 1.0 nm scanning window

Most reported marine adhesives consist of protein complexes dispersed in a polysaccharide matrix (Hennebert et al. 2008), probably due to the multifunctionality and diversity of protein. A study done by Callow et al. showed that algal spores become less sensitive to detachment after treatment with proteolytic enzymes (Callow et al. 2000), indicating the key role of proteins in attachment. Some proteins in adhesives have important biochemical characteristics, such as being rich in polar and charged residues, which presents a significant number of functional

groups for cross linking and adhesion. A recently identified barnacle cement protein is a surface-coupling protein (Mrcp-19 k) which could efficiently adsorb to surfaces with various characteristics, regardless of charge and hydrophobicity (Urushida et al. 2007).

## High adhesion strength of ivy nanoparticles

As observed in the above biological adhesives, the existence of a large amount of proteins in the form of nanoparticles implies that they play an important role in attachment. However, direct evidence for the adhesion ability of these nanoparticle-dominated adhesives has not been obtained. After confirmation of the existence of nanoparticles from cultured ivy rootlets, its adhesion force was studied for the first time using AFM. After calibration and determination of the deflection sensitivity and force constant of the AFM tip, force versus distance curves were performed to measure the pull-off force generated from the interaction between the tip and the adhesive. Thirty successful approach-retract curves of freshly prepared ivy adhesive samples were conducted to determine the optimal adhesive force. Out of these curves, the values of pull-off force ranged from 274 to 307 nN, with an average value of 298 ± 8.34 nN. A typical force curve exhibited a single pull-off event during the measurements (Fig. 2a), even though saw-toothed curves were observed occasionally (Fig. 2b). The saw-toothed pull-off is typical of polymer-based materials, and indicated that the tip was interacting with multiple components of the nanocomposite adhesive.

The nano-scale adhesion force for freshly released ivy adhesive averaged 298 nN, which is four times greater than what could be measured for the adhesive from algal spores using AFM (Callow et al. 2000). However, the readings are close to a recent study of adhesion force between a polystyrene nanoparticle and a nanofiber in the range of 159.5–384.9 nN (Xing et al. 2010). Also, to ensure that the measured force was not due to the tip contamination, the tip was frequently moved to a bare silicon surface to calibrate the pull-off force. The force measured on the bare silicon wafer surface was around 30 nN, which is comparable to previous reports (Grinevich et al. 1999).

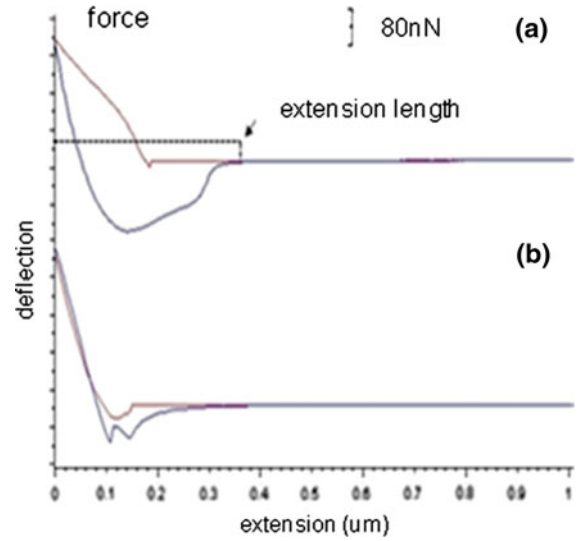


**Fig. 2** A typical approach-retract cycle illustrates the adhesion profile and other mechanical properties of ivy nanoparticles examined under AFM in **a**. Saw-toothed curves were occasionally observed in **b**

## High elasticity of ivy nanoparticles

The addition of filler materials to adhesives normally strengthens the adhesive, but reduces the tack which is a required character for permanent attachment. The addition of a nanomaterial, however, showed different behaviors, exhibiting an increase in both strength and tack (Wang et al. 2006), which might explain the advantage of nanoparticles for strong attachment. Tackiness theory predicts that as the elastic modulus of the coating increases, the tack energy decreases (Gay and Leibler 1999). The different tack performance from nanomaterial fillers might be due to their unusual interactions with polymeric matrix, which increases the elastic modulus of the composite adhesive. For this purpose, we examined the elasticity of the ivy adhesive. In this study, the slope of the approach curve was used to calculate Young's modulus. The obtained Young's modulus through this method ranged from 1.035 to 1.297 GPa for the ivy adhesive, and was much greater than what was calculated for algal spores. Young's modulus of the dried adhesive was comparable to a hard material such as rubber, nylon, and some plastics. High elasticity of the ivy nanocomposite could be attributed in part to the Hall–Petch effect, which predicts that as grain size

decreases into the nanometer range, stiffness increases due to increased trapping of dislocations at interfaces (Waychunas and Zhang 2008).

## Time-based loss of adhesion

The time from initial secretion of the adhesive to permanent attachment is a slow process that involves corresponding changes in the adhesive. These changes could be due to water evaporation after secretion, or chemical changes due to polymerization. Ultimately the changes will be reflected in the hardening of the adhesive, which are believed to correspond to the formation of strong permanent attachment. To follow the change in adhesive properties over time, force versus distance curves were taken over the course of 24 h. The time-course of adhesion revealed a slow reduction in the first 8.5 h from 298 to 202 nN, followed by a constant level after 24 h (Fig. 3). A 30.2% decrease of adhesion force was observed over a curing period of 8.5 h. This change was not as great when compared to a 65% decrease observed during the first hour of settlement in the adhesive secreted from *Enteromorpha*, an algae (Callow et al. 2000).

One explanation for the decreased adhesive force was the hardening of the limited amount of polymer matrix material in the ivy adhesive. As observed with many polymer glues, the hydrated form has a high adhesive strength, whereas the dried form lacks any adhesion. This is due to a change in conformation of the material and the gradual formation of a solid upon drying. Another explanation includes the loss of capillary forces due to the decreased water content during the drying process. Capillary forces play a significant role in the adhesive force of the gecko, and decreased relative humidity has been related to decreased adhesion force (Sun et al. 2005). The freshly released adhesive contains a significant percentage of water which is lost as the sample dries. The capillary forces associated with water in the hydrated state would become smaller during the drying process, leading to the decreased adhesion force.

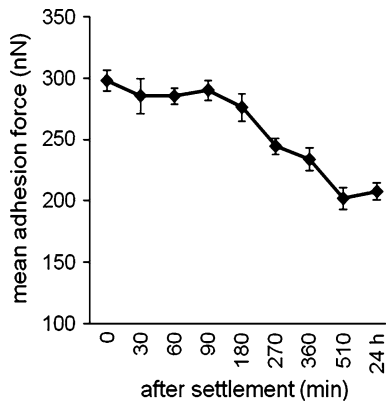


**Fig. 3** Change of adhesion force within 24 h. The force was measured at various time points after deposition. Each point represents an average of 30 retraction curves ±95% confidence limits

## Limited change in extension length and Young's modulus

The decreased force over time can be due to the existence of polymeric matrix and be related to changes of elasticity and extension length as observed in previous studies (Callow et al. 2000), which is also a typical response for liquid adhesives during the hardening process. Because of the existence of a small amount of polymeric matrix in ivy adhesive, it is expected similar changes exist during the hardening process of the adhesive. For this purpose, elasticity and extension length for the ivy adhesive were also investigated over the 24-h time-course. From Figs. 4 and 5, we concluded that the curing profiles of the ivy adhesive were consistent with the pattern observed from the adhesive of the algae *Enteromorpha* (Callow et al. 2000), but at a much lower degree. The values for extension length (interpreted in Fig. 2a) show a limited decrease over 24 h, indicating a minimal hardening over the time-course. Correspondingly, Young's modulus increased by 20.2% over 6 h, much less than normally found in liquid or soft polymer adhesives (Callow et al. 2000). This observed difference in extension length and Young's modulus change over time was most likely due to the low percentage of polymeric matrix. The existence of a large amount of nanoparticles, on the other hand, does not change in elasticity and extension length during the hardening process. The fact that polymeric adhesives, such as tape, are soft and deformable allows for intimate contact over a relatively large surface area making these adhesives optimal to explore the sub-atomic distance of van der Waals force (Gay and Leibler 1999). The strong curing process in normal liquid adhesives works well when contact surfaces are

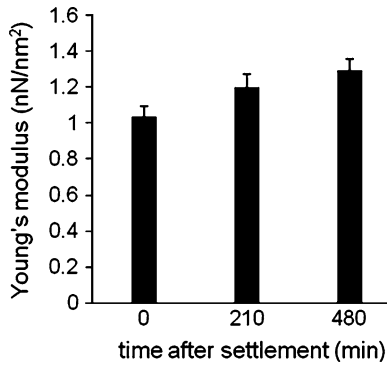


**Fig. 4** Increased Young's modulus value for ivy nanoparticles. Each point represents an average of 30 approach curves ±95% confidence limits

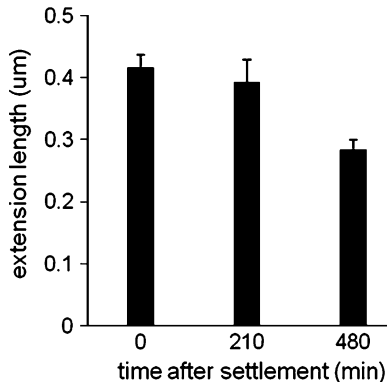


**Fig. 5** Decreased extension length for ivy nanoparticles. Each point represents an average of 30 retraction curves ±95% confidence limits

smooth. However, as in the case of ivy, the attaching surfaces for these plants are extremely hard, rough, and irregularly shaped. The strong curing process in the contact areas will lead to the notably decreased volume thus the decreased contact area of the rootlets with attaching surfaces. The limited curing process in ivy adhesive thus works to maintain the maximal contact areas through nanoparticle part, and facilitate intimate contact and van der Waals interactions through deformable matrix part.

## Mechanics model of ivy nanoparticle adhesion

As studied in marine adhesives, different mechanisms might exist for strong attachment of nanoparticle components. Because of its strong attachment to surfaces of different physical and chemical properties, van der Waals force is of priority to be investigated. A recent study proposed three mechanical models to explain the strong adhesion of ivy nanoparticles to a rigid substrate based on van der Waals force (Wu et al. 2010). The selection of a specific model depends on the contact angle and mechanical properties, especially Young's modulus, of the nanoparticles. Based on the Young's modulus obtained from this study, we have chosen the Johnson–Kendall–Robert (JKR) model. JKR theory was created to characterize the adhesive contact between elastic spheres based on van der Waals force, and is applicable to large, soft, and compliant materials with high surface energy (Johnson et al. 1971). The theory can be applied to various conditions occurring between the ivy nanoparticles and substrate surfaces. Equation (1), based on JKR theory, describes the method to calculate the pull-off force of an elastic sphere in contact with a rigid substrate; essentially a model for the contact between an ivy nanoparticle and a solid surface.

$$F_{\mathrm{p}} = \sqrt{8\pi E^{*}\omega R^{3}\sin^{3}\alpha} \tag{1}$$

In Eq. (1), $E^{*}$ is the effective Young's modulus, $R$ is the radius of the particles, and $\alpha$ is the contact angle. $\omega$ is the work of adhesion, and can be calculated as:

$$\omega = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

where $\gamma_1$ and $\gamma_2$ represent the surface energy of the two surfaces, and $\gamma_{12}$ is the interface energy between the two materials. The value of $\omega$ is set here as 0.025 J/m$^2$ as previously discussed (Wu et al. 2010).

Based on these equations, the adhesion force for spherical nanoparticles with different effective Young's moduli was calculated at two different contact angles of 30° and 45°. As shown in Fig. 6, a larger contact angle translates to a larger contact area, which provides a stronger adhesion force for each individual nanoparticle. Similarly, for material with a larger Young's modulus, there will be a stronger van der Waals force formed between nanoparticles and the surface. From the calculated value of Young's modulus for ivy nanoparticles, between 1.035 and 1.297 nN/nm$^2$ (GPa), this model indicates that van der Waals force alone could provide forces in the range of 55 to 110 nN, depending on actual value for Young's modulus and the contact angle of these nanoparticles to the surface.

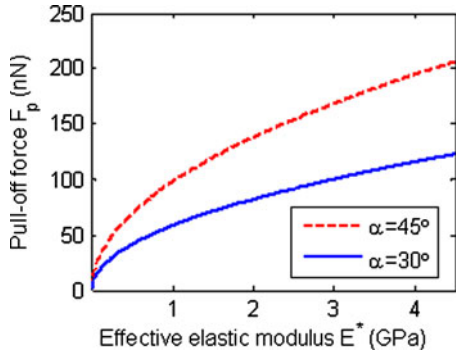


**Fig. 6** Curves from the mechanics model of adhesion force between nanoparticles and the substrate for materials with different Young's modulus and at two contact angle of 30° (*solid line*) and 45° (*dashed line*)

The exact chemical composition of the ivy nanoparticles is currently under investigation, and the mechanism that contributes to the strong adhesion will be more accurately interpreted and investigated upon collecting this data. However, calculations based on JKR theory indicated that van der Waals force alone would provide ~100 nN of force for the nanoparticles, which is 1/3 of what was measured using AFM. This difference indicates that chemical or mechanical interactions other than van der Waals force are involved in ivy adhesion. These possible interactions include capillary forces, hydrogen bonding, electronic forces, or even cross linking of the matrix with attaching surfaces (Israelachvili 1992).

## Conclusions

This study used AFM to characterize the structural and mechanical properties of the nanocomposite adhesive from cultured ivy rootlets. The adhesive from cultured rootlets was examined and found to maintain the similar structure of nanocomposite as the naturally grown ivy rootlets. The nanocomposite adhesive was then examined for adhesion strength using AFM. The average force for the fresh adhesive was found to be 298 nN. This force was comparable to other reports of nanoparticle–nanofiber adhesion, but four times larger than the adhesion strength of algal adhesive. The mechanical properties of the ivy adhesive were also investigated, and a large value of Young's modulus was observed for the nanocomposite adhesive, explaining the strong tackiness of the ivy adhesive. In addition, the curing process of the ivy adhesive was tracked over 24-h. The limited curing process of the ivy adhesive helps fill gaps in the attaching surface, leading to more intimate contact and increased van der Waals interactions with the surface. A theoretical study based on van der Waals force of ivy nanoparticles was performed, and it was found that other forces exist that contribute to the strong attachment of ivy rootlets except van der Waals force. This study has provided first-hand experimental data to display and analyze one of the strongest adhesives in nature. Future study will focus on understanding interactions of ivy nanoparticles each other and with the adhesive matrix using functionalized AFM tips.

**Acknowledgments** This research is sponsored by the US Army Research Office, Life Sciences Division, Biochemistry Program under the contract W911NF-10-1-0114. We would like to thank Susan Brocker for her assistance with the tissue culture work. Burris and Stewart's work are partially funded by the Tennessee Agricultural Experiment Station.

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