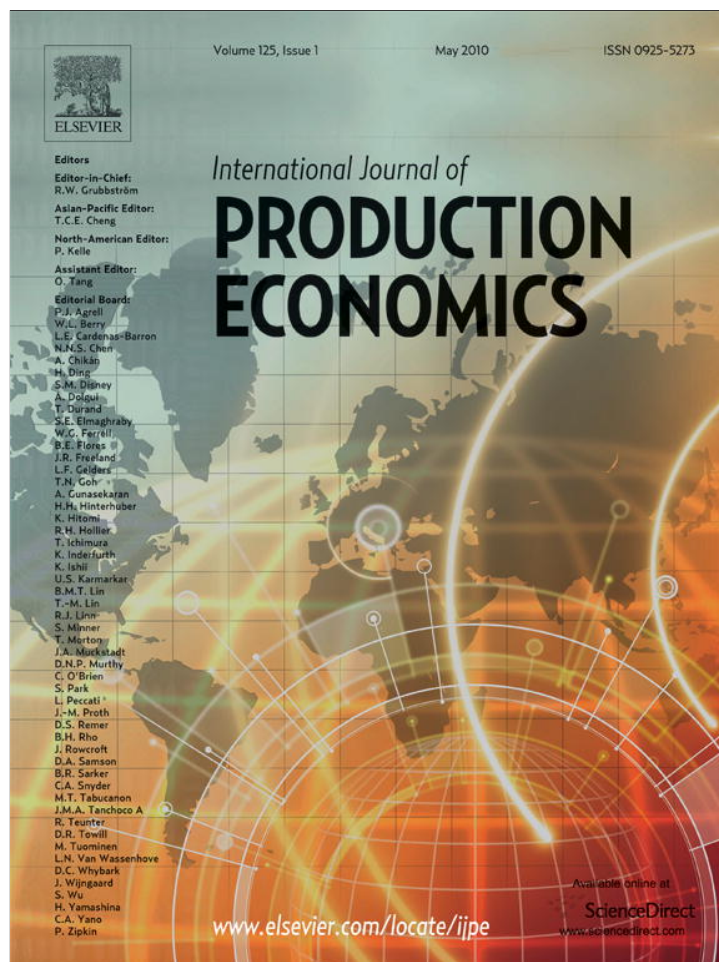


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The effect of surface roughness on adhesive properties of acrylate copolymers

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ABSTRACT

The effect of surface roughness on the adhesive properties of statistical, uncrosslinked butyl acrylate–methyl acrylate copolymers with different molecular weights ($M_w=54\,000$, $192\,000$, and $600\,000$ g/mol) has been investigated using a combination of probe tack test and simultaneous video-optical imaging. Steel probes with different average surface roughnesses ($R_a=2.9$, 41.2 , and 291.7 nm) have been used.

The debonding process in a tack experiment is mainly controlled by the viscoelastic properties of the polymer, which control deformation and break of fibrils. However, increasing the probe surface roughness leads to a decrease of the maximum force during debonding and, correspondingly, the work of adhesion in a tack experiment decreases. Surface roughness has a strong effect on the initial cavitation process. The total number of cavities increases with increase in roughness, while their size decreases. The number of cavities increases slowly at the beginning of debonding, then rapidly increases as the force increases, and finally levels off, when the maximum force is reached. Two types of cavities are observed during debonding. Cavities of the first type appear at the beginning of debonding and their size increases slowly, while cavities of the second type appear at a higher stress level, when peak in force is approached, and their growth rate is about five times higher than that of cavities of the first type. Cavities even grow when the force has passed its maximum and eventually stop growing when the characteristic stress plateau is reached. Nevertheless, the growth rate for both cavity types is found to be independent of the surface roughness, but it is controlled by the viscoelastic properties of the polymers used and, accordingly, it decreases significantly with increase in molecular weight.

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1. Introduction

Pressure sensitive adhesives (PSAs) represent a class of materials of great interest in recent years due to their wide application in industry and everyday life. The main property of such materials is that they can adhere to any surface under low (1–10 Pa) contact pressure and short (1–5 s) contact time without any change of temperature or chemical reaction [1]. This property of PSAs is called tack. A tacky material has to be sticky to the touch; therefore all testing methods of tackiness have a goal to reproduce in one way or another the test of a thumb being brought in contact and subsequently removed from the adhesive surface [2,3]. The probe tack test with a flat cylindrical probe [2,3] is widely used to test short-time and low-pressure adhesion. The test has an advantage of applying uniform stress and strain rate to the adhesive film over the whole surface of the probe. Addition-

ally, microscopic analysis of the sequence of events occurring during the tack test is necessary to attempt a detailed interpretation of a tack curve and to better understand the debonding mechanism. Several experimental parameters such as temperature, contact time and contact pressure can be varied in the probe tack test and these parameters can considerably change the fracture mechanism [4,5]. Molecular parameters of an adhesive, such as molecular weight, polydispersity and degree of cross-linking, also determine the adhesion behavior of PSAs [2,6].

Although by definition PSAs are designed to stick to any surface and supposed to be practically insensitive to the surface of adherent, it is obvious that interface properties also can influence the adhesion of PSAs. The debonding of PSAs from a probe in a tack test leads to the formation of cavities that first grow in a PSA film and then become elongated to form a fibrillar structure. An earlier investigation of the mechanism of failure of PSAs on model acrylate based PSAs has shown that the formation of cavities occurs at or near the interface between the probe and the film [7]. Therefore it is reasonable to suggest that the roughness of the surface, either of the adhesive film or of the probe, can be an important parameter affecting the adhesion of PSAs. In an early

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study Zosel [8] pointed out that the work of adhesion or fracture energy significantly depends on the probe surface roughness as long as the contact area is not completely wetted, which is especially the case for low contact forces, short contact time and high polymer modulus. A limiting value for the work of adhesion was found only at contact times longer than the disentanglement time of the polymer. The effect of surface roughness on the adhesion of PSAs has also been discussed theoretically [4,9,10] and it was proposed that the adhesion on the rough surface is limited due to the absence of full surface contact. The model of Creton and Leibler [4] predicts that the true contact area and hence the work of adhesion are proportional to the inverse of the shear modulus $G(t)$ of the polymer. In an experimental study [11] on styrene–isoprene–styrene triblock copolymers using steel probes of two different roughnesses ($R_a=0.05$ and $1\ \mu\text{m}$), it was shown that the number of cavities formed during debonding strongly increases with increase in roughness and the whole debonding process is affected by the roughness. At low temperature, when the stress within the polymer film does not relax during the time of contact, tack decreases with increase in roughness; the opposite behavior is found at high temperature, when the stress in the adhesive layer fully relaxes during contact time. Results of a systematic study regarding the role of surface roughness on the adhesion of model acrylic latex are reported in [12]. Five different probes with surface roughnesses in the range from $R_a=11$ to $148\ \text{nm}$ were used. It was found that extensive cavitation sets in at the maximum of the nominal stress, and this stress peak decreases with increase in roughness. Furthermore, the authors claim that the rate of cavity expansion corresponds to the slope of the stress vs. strain curve, which decreases as roughness increases. Cavity growth during debonding has been studied in more detail using video-imaging [13], revealing that cavitation starts at a stress level far above the elastic shear modulus of the polymer, and cavities grow exponentially at a strain rate much higher than the applied external rate.

A characteristic difference between cavitation and cavity growth on smooth and rough surfaces was pointed out in [14]. On a rough surface, cavitation starts from existing contact defects and all cavities grow simultaneously at the same rate, whereas on a smooth substrate cavities occur sequentially and their growth rate increases with increase in stress level at which they are released.

The present paper deals with a detailed investigation of the influence of surface roughness on the debonding process during a tack experiment. Uncrosslinked butyl acrylate–methyl acrylate copolymers are used as model PSAs. The probe tack test is combined with a simultaneous video-image analysis and three steel probes of average surface roughness between $R_a=2.9$ and $291.7\ \text{nm}$ are used. Our experimental setup allows for observation of the debonding process and corresponding cavity formation in situ with high spatial and temporal resolution, images of the contact area of the probe with the PSA film are simultaneously recorded with the contact force at any stage of the tack test. The quality of the obtained images enables us to obtain reliable results for the number and size of cavities formed. This also allows for a study of the kinetics of cavitation in detail and to evaluate the influence of surface roughness on the cavity growth rate. Finally, we discuss our results in comparison with previous investigations.

2. Experimental

2.1. Materials

The PSAs used in this study were model statistical acrylic copolymers with different molecular weights. The model

copolymers p(nBA-stat-MA) were polymerized in methylethylketone (MEK) at $80\ ^\circ\text{C}$ (low and intermediate molecular weight samples) or in *n*-butyl-acetate at $80\ ^\circ\text{C}$ (high molecular weight sample). The copolymers contained 80% butyl acrylate (BA), 20% methyl acrylate (MA). The average molecular weights M_w of the copolymers determined by GPC were $54\ 000$, $192\ 000$, and $600\ 000\ \text{g/mol}$, and their polydispersities M_w/M_n were 3.9, 6.4, and 13.6, respectively. The copolymers with $M_w=54\ 000$ and $192\ 000\ \text{g/mol}$ were supplied as 71% and 80% solutions in MEK, respectively. Copolymer with $M_w=600\ 000\ \text{g/mol}$ was delivered as 49.4% solution in *n*-butyl-acetate.

Transparent glass slides ($200 \times 50 \times 3\ \text{mm}$) were purchased from Hera Glas GmbH, Germany. Abrasive papers were purchased from Bühler GmbH, Germany. Acetone was purchased from Carl Roth GmbH+Co. KG, Germany. The probes used for the tack measurements were flat-ended cylinders with a diameter of $5\ \text{mm}$ made of stainless steel, type 1.4034 (Alois Schmitt GmbH & Co. KG, Germany).

2.2. Methods

2.2.1. Rheological measurements

Rheological measurements were performed on a rotational rheometer RS-150 (ThermoHaake GmbH, Germany) using cone and plate fixtures (cone diameter: $20\ \text{mm}$; cone-angle: 1°).

2.2.2. PSA film preparation and characterization

For our experiments we used $50 \pm 5\ \mu\text{m}$ thick adhesive films prepared by casting the PSA solutions onto clean glass slides using a home-made doctor blade with a gap in a combination with an automatic film applicator coater ZAA 2300 (Zehntner GmbH, Switzerland). The coating speed used for the film preparation was varied from 10 to $25\ \text{mm/s}$. The coating speed had practically no influence on the film thickness, but the constant speed was found to be very important for obtaining uniform PSA films with a reproducible film thickness. For the samples studied in this work we used a coating speed of $20\ \text{mm/s}$. Freshly prepared films were stored at room temperature overnight (for at least $12\ \text{h}$) to allow slow solvent evaporation without bubble formation, and subsequently at $120\ ^\circ\text{C}$ for $1.5\ \text{h}$ to evaporate the remaining solvent and to obtain a smoother polymer surface.

The PSA film thickness was determined by two independent methods. According to the first method the film thickness was measured by a dial gauge with a flat-ended feeler using silicon paper to avoid the adhesion of the feeler to the film. Alternatively, the film thickness was determined from a force–distance curve obtained from a tack measurement. The distance was calibrated to zero at the surface of the glass substrate. The difference between the known substrate position and the position, at which the first contact with polymer material takes place, i.e. the position at which the first negative force value is detected, gives information about the film thickness. Both methods provided similar results.

The composition of the investigated PSA films was studied using X-ray reflectivity [15]. The measurements were performed with a Siemens D5000 Diffraktometer (Siemens AG, Germany) at room temperature. The reflectivity curves and the corresponding fits are plotted (Fig. 1a) in Fresnel-normalized representation. As a result of the data analysis the refractive index profiles (Fig. 1b) perpendicular to the sample surface can be extracted. Since only two components are involved and the refractive index is proportional to the electron density, one can read this as a composition profile. The horizontal lines mark the values of the involved homopolymers and the statistical copolymer as shown by the label. The composition of the PSA films near the surface differs from the

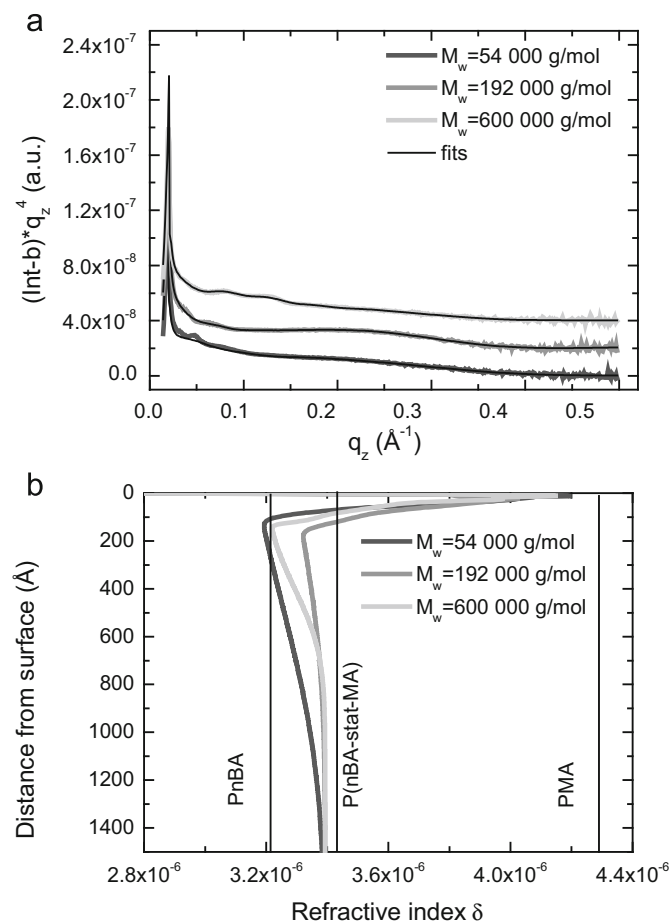


Fig. 1. X-ray reflectivity data and corresponding fits in Fresnel-normalized representation of BA/MA films of three molecular weights (a) and corresponding refractive index profiles of the surface-near region of the shown fits (b).

composition in the bulk film. The latter is the average composition of the copolymer, which is 80% PnBA and 20% PMA (neglecting the small amount of photoinitiator). At the surface, however, a thin enrichment layer of PMA is detected. This is followed by an enrichment region of PnBA with a thickness of approximately 100 nm before the homogenous bulk composition is reached.

2.2.3. Probe preparation and characterization

To prepare the probes with various surface roughnesses the stainless steel probes were polished to different degrees with abrasive papers. The first probe was polished with abrasive papers number 80 and 120. The second probe was polished with abrasive papers number 320 and 600. The third probe was polished first with abrasive papers number 320, 600, 1000, 4000 and finally with a diamond dispersion (diameter of particles 1 μm).

A white light confocal microscope NanoFocus $\mu\text{Surf}^{\text{R}}$ was used for the characterization of the curvature of the flat end after the polishing procedure. The profile along the whole diameter of the probe was measured. Polishing can lead to a roundness of the edges and, therefore, to a convex curvature, which does not allow one to achieve homogeneous contact pressure during the tack measurement. To avoid the convexity the probe was fixed during polishing in a special holder. In this work we used only probes with flat profiles.

Q-ScopeTM Scanning Probe Microscope (SPM) (Ambios Technology Inc., USA) was used for the characterization of the probe surfaces. The SPM images were carried out in a Contact Mode using silicon contact tips CSC17 (MikroMasch, Estonia) with a tip

radius of about 10 nm. Fig. 2 shows typical SPM images of the probe surfaces of different roughnesses and also the profiles taken from the SPM images at the positions shown by lines on the images. From these profiles the average surface roughness R_a was determined as an average deviation from the mean surface plane. It has to be noticed that the probe surfaces have peak to valley distances far smaller than the adhesive film thickness.

2.2.4. Tack experiment and video-optical observation

Fig. 3 shows an experimental setup used for the tack measurements. The setup is based on the commercial device Texture Analyzer TA.XTplus (Stable Micro Systems, UK) modified with a quartz force sensor (Kistler Instrumente GmbH, Germany) with a force range ± 500 N and a threshold of 1 mN. This quartz sensor has much less compliance than the original strain gauge load cell of the Texture Analyzer TA.XTplus, it is specified with a stiffness of 15 N/ μm . Preliminary experiments have shown that the compliance of the whole mechanical setup including the force sensor is negligibly small compared to that of the PSA film. This is essential for a reasonable force measurement especially at the initial stage of debonding. The glass slide with the deposited PSA film is positioned on the home-built vacuum table below the probe, which is connected to the platform attached to the base of the Texture Analyzer. By using the screws of the platform one can precisely adjust the position of the table surface and, consequently, the surface of the sample parallel to the surface of the probe. The probe tack tests were performed as follows: The probe approached the sample with a rate of 0.1 mm/s, contacted the adhesive film with a specified contact force and was held at a constant position for 1 s. The contact force was varied from 3 to 20 N, corresponding to contact pressures from 0.15 to 1.02 MPa. The probe was then withdrawn with a constant rate of 0.1 mm/s. The resulting force–distance and force–time curves were recorded simultaneously with video images of the contact area. Testing was performed at a temperature of 22 $^{\circ}\text{C}$. The surface of the probe was cleaned with acetone before each test. To obtain reliable average values each sample was tested five times.

Fig. 4 shows a typical stress vs. strain curve during the debonding of PSA and video images of contact area at certain moments and corresponding schematic side views, illustrating the stages of debonding mechanism. The probe tack test and the corresponding debonding mechanism have been described in detail before [2,16]. Briefly, there are several stages:

1. bonding to the surface of adhesive material;
2. *first stage of debonding*: initiation of the failure process through the formation of cavities at the interface (maximum of the stress vs. strain curve);
3. *second stage of debonding*: lateral growth of the cavities in the plane of the film;
4. *third stage of debonding*: growth of the cavities in the direction normal to the plane of the adhesive film (fibril formation) resulting in a plateau in the stress vs. strain curve;
5. *separation of the surfaces*: adhesive or cohesive failure.

From the stress vs. strain curve the stress peak σ_p and the deformation at break ε_B were determined. The measured force F was converted to a nominal stress $\sigma = F/A_0$, where A_0 is a true initial contact area, measured from the optical images, taken at the beginning of the pull-off stage. The tack value was obtained from the area under the nominal stress vs. nominal deformation (strain) curve. The latter was calculated from real-time film thickness h as $\varepsilon = (h - h_0)/h_0$, where h_0 is the initial film thickness.

The video images were obtained with a high-speed camera KL MB-Kit 1M1 (Mikrotron GmbH, Germany) used in a combination

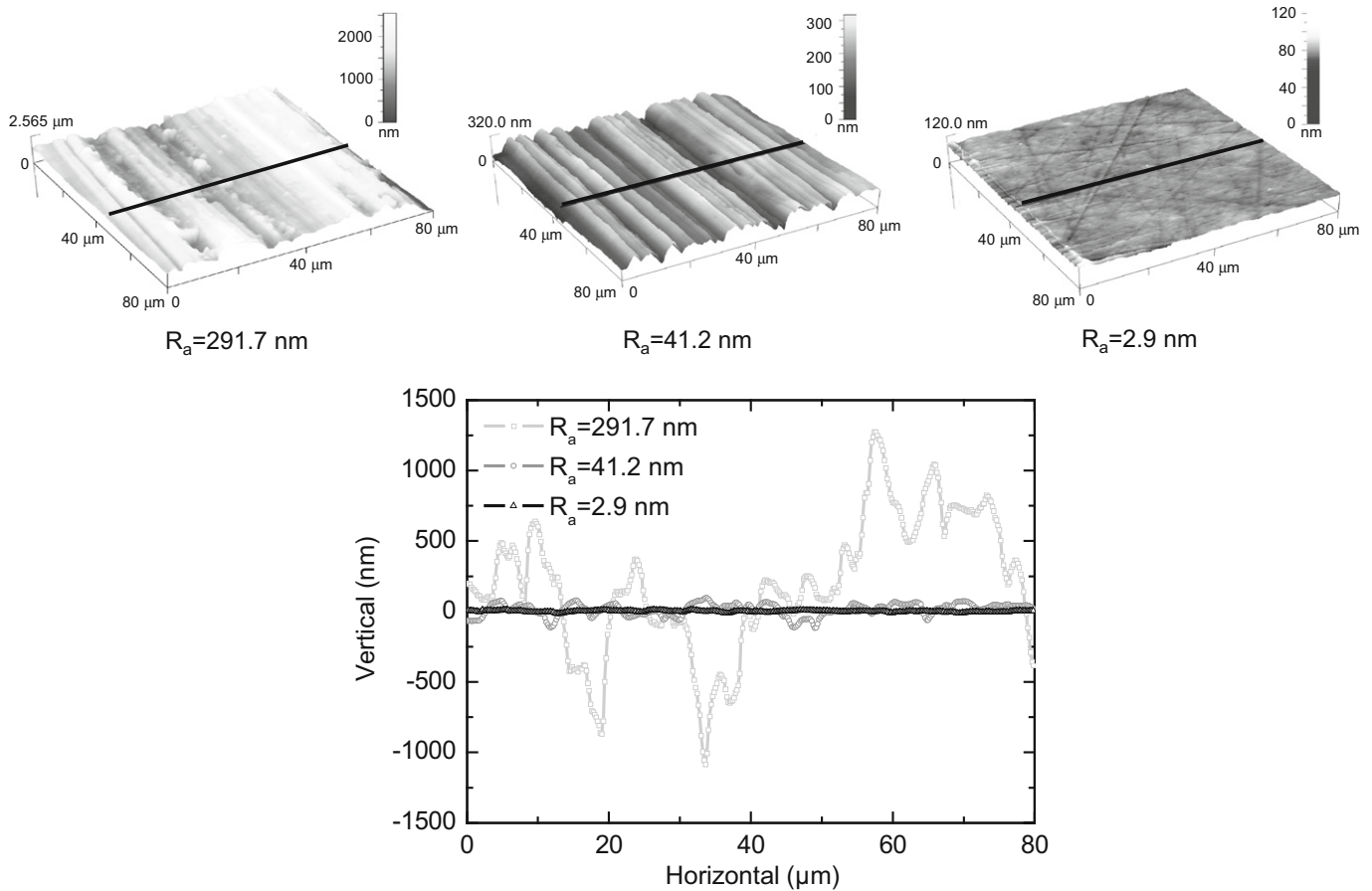


Fig. 2. SPM images of the probe surfaces and profiles.

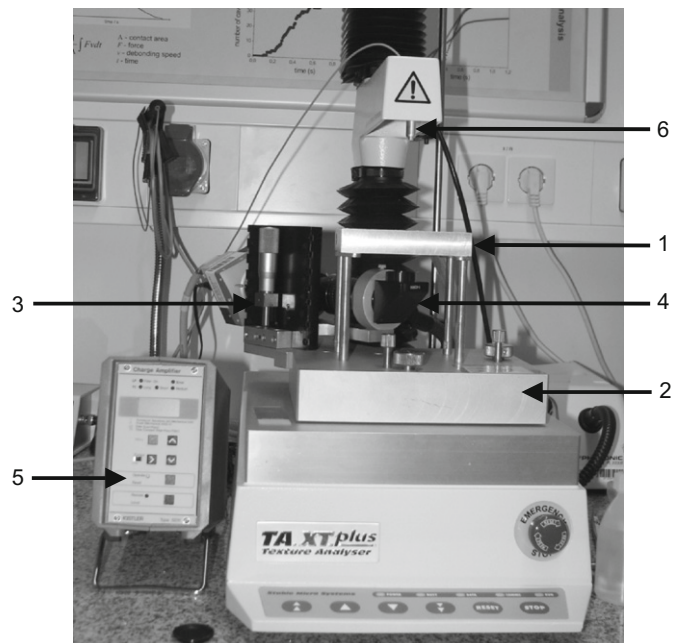


Fig. 3. Experimental set-up for tack measurements and video-optical observation: 1—vacuum table; 2—platform; 3—video camera; 4—objective 90° zoom; 5—charge amplifier; 6—probe.

with zoom 90° KL-Z6 and cold light source KL3000B. The camera allows recording 124 frames/s at a maximum resolution of 1280 × 1024 pixels (1 pixel is approx. 5 μm). The camera was

mounted below a hole in the surface of the vacuum table under the glass slide supporting the adhesive film.

The force–time curve was synchronized with the video sequence in such a way that the first contact of the probe with the sample in the force curve corresponds to the image showing the first contact (the first image recorded corresponds to the moment when it was observed that the probe touches the surface of the polymer film). The videos were quantitatively analyzed using Visiometrics Image Processing System software (Prof. Dr. Stephan Naser, University Darmstadt). The true contact area and growth rate of individual cavities were determined.

3. Results and discussion

3.1. Rheological characterization

In order to estimate the performance of the studied polymers as PSAs we carried out rheological tests. Fig. 5 shows the shear moduli G' and G'' as a function of frequency for BA/MA copolymers of three molecular weights. The data were measured at different temperatures between 2 and 120 °C and shifted to the reference temperature $T_{ref}=23$ °C according to the time–temperature superposition principle [17]. It is well known that there is a correlation between the adhesion performance and the bulk viscoelastic properties of PSAs [1]. All PSA applications involve bonding and debonding steps. Bonding is a low rate process and it is the result of the adhesive being able to flow and wet under light pressure. Therefore, it can establish a contact with a substrate. Debonding is a high rate process and it is a deformation of the adhesive under stress, followed by the

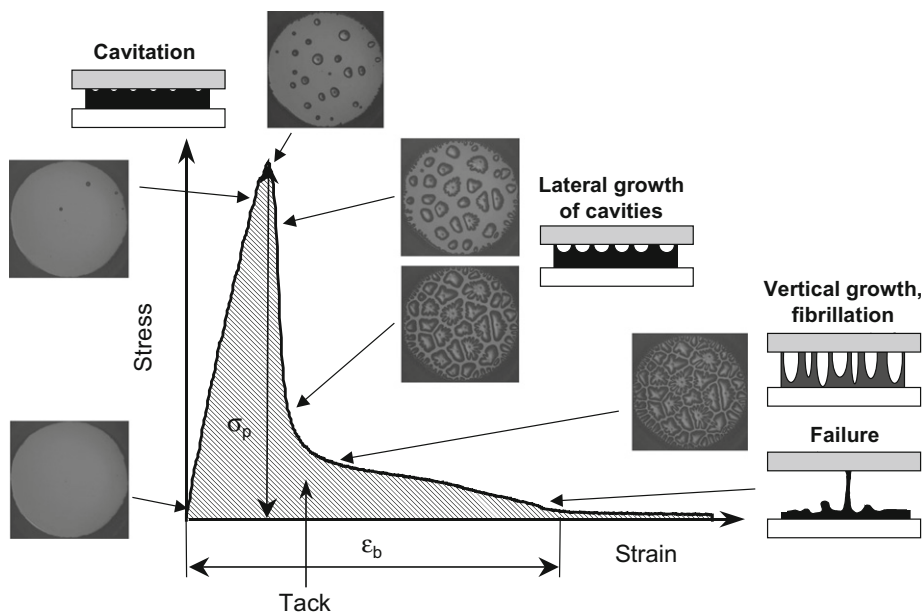


Fig. 4. Schematic of a stress vs. strain curve, schematic side views, illustrating the stages of debonding mechanism and the corresponding representative images of contact area for BA/MA PSA with $M_w=192\,000$ g/mol measured with probe of $R_a=2.9$ nm. The tack or work of adhesion is represented by the shaded area.

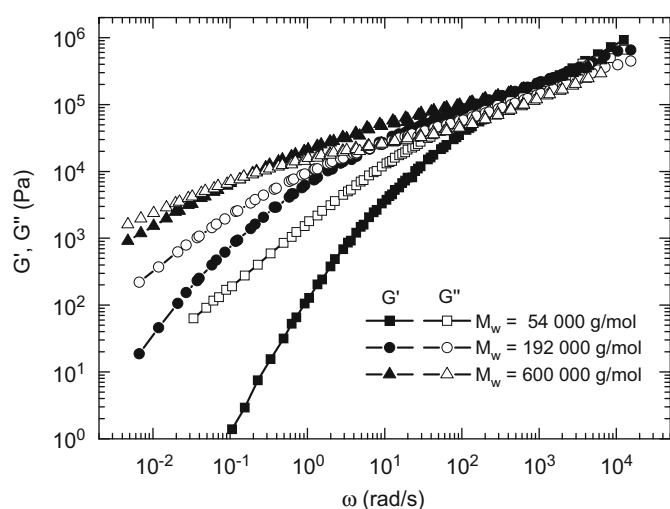


Fig. 5. Shear modulus (G' —storage modulus; G'' —loss modulus) as a function of frequency for BA/MA PSAs.

separation from the substrate. At this stage the adhesive should be cohesive and internally strong. Bonding corresponds to low oscillatory frequencies and debonding to high frequencies. Therefore, for PSAs the viscous modulus should predominate ($G'' > G'$) at low frequencies, and the elastic modulus should predominate ($G' > G''$) at high frequencies [18]. The requirements for the performance of PSAs have been described in the criterion reported by Chu and Dahlquist [18,19]. According to Dahlquist's criterion of tack, at low frequencies G' should be below 10^5 Pa. All studied polymers fulfill the Dahlquist criterion; therefore they can be used as PSA model systems. As expected, the increase of molecular weight leads to an increase of the longest relaxation time (characterized by the crossover of G' and G'') and accordingly to an increase of G' and G'' at low frequencies. At high frequencies the G' , G'' curves for samples of different M_w superimpose, since stress relaxation is controlled by short range chain motion, which is independent of molecular weight. The frequency dependence of the linear viscoelastic moduli observed here is typical for linear,

flexible polymers and there is no indication of occasional thermal crosslinking of the polymers. Generally, the tack of a polymer is related to the linear viscoelastic moduli in the frequency range between 1 and 100 s^{-1} ; here we apply relatively low debonding velocities corresponding to a characteristic strain rate of $\approx 1\text{ s}^{-1}$. In this frequency range the viscoelastic signature of our model systems changes from predominately elastic at the highest M_w to predominately viscous at the lowest M_w , while $G' \approx G''$ for the intermediate M_w .

3.2. Tack

As was already mentioned above, some experimental parameters, e.g. temperature, contact time and contact pressure, can be varied in the probe tack test and they can influence the test results. Therefore, in order to study the effect of surface roughness on the behavior of PSAs, it is necessary to fix all experimental parameters. Fig. 6 shows the effect of contact pressure on the tack values for BA/MA PSAs. The contact pressure was calculated from the measured contact force and real contact area, determined from the images. One can see that for all studied PSAs the tack values increase with increase in contact pressure independent of the roughness of the probe used. It has to be noticed that in contrast to earlier investigations [20], no limiting value for the tack is reached, because unlike commercial PSAs the polymers used here are not crosslinked. It should be mentioned that under the experimental conditions chosen here the failure is always cohesive as expected for non-crosslinked polymers. The variation of tack with contact pressure is more or less independent of molecular weight or surface roughness, and thus the contact pressure was fixed at 0.51 MPa in all subsequent measurements.

Fig. 7 shows representative stress–strain curves for the three studied polymers obtained with probes of three different roughnesses. Fig. 8 shows the dependence of the parameters, calculated from these curves, i.e. stress peak, deformation at break and tack on the probe roughness. From Fig. 7 one can see that, first, for the probes of all surface roughnesses studied, the peak in nominal stress is always present. This result is in contradiction to a previous study [14], where no nominal stress peak in case of a rough interface was observed. Secondly, the stress peak value

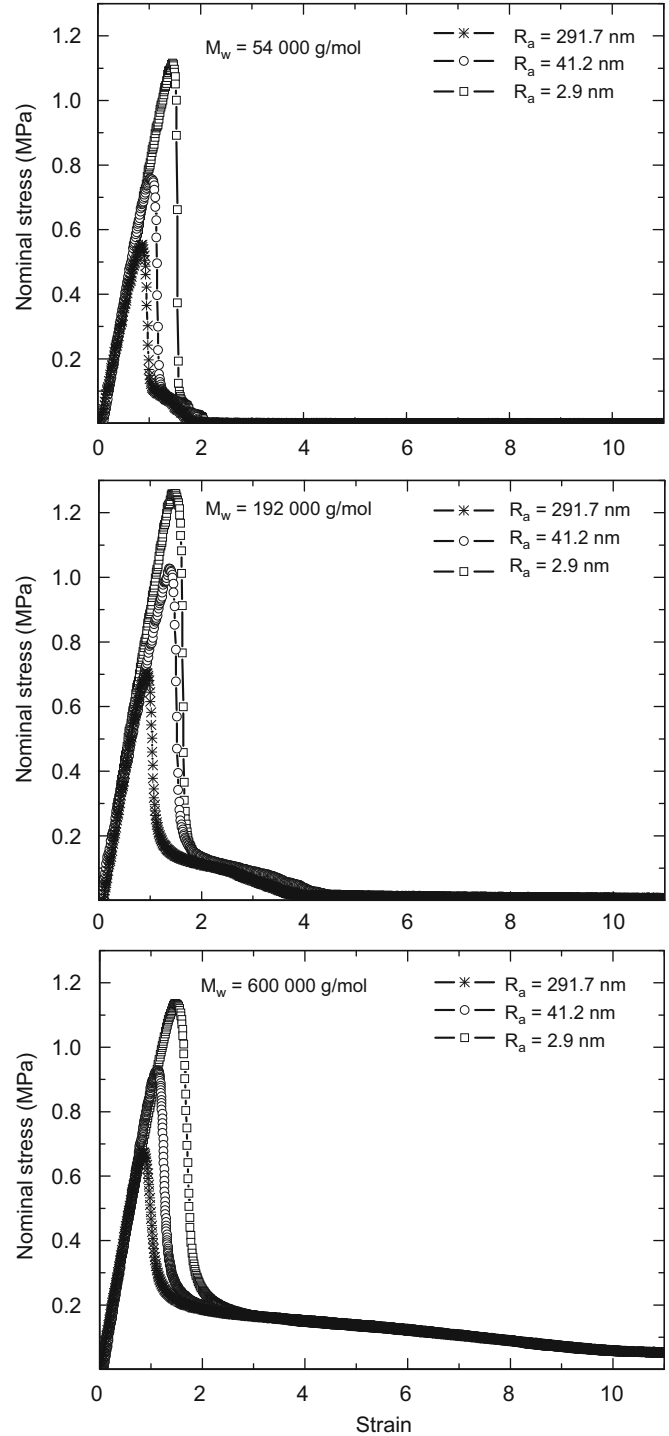
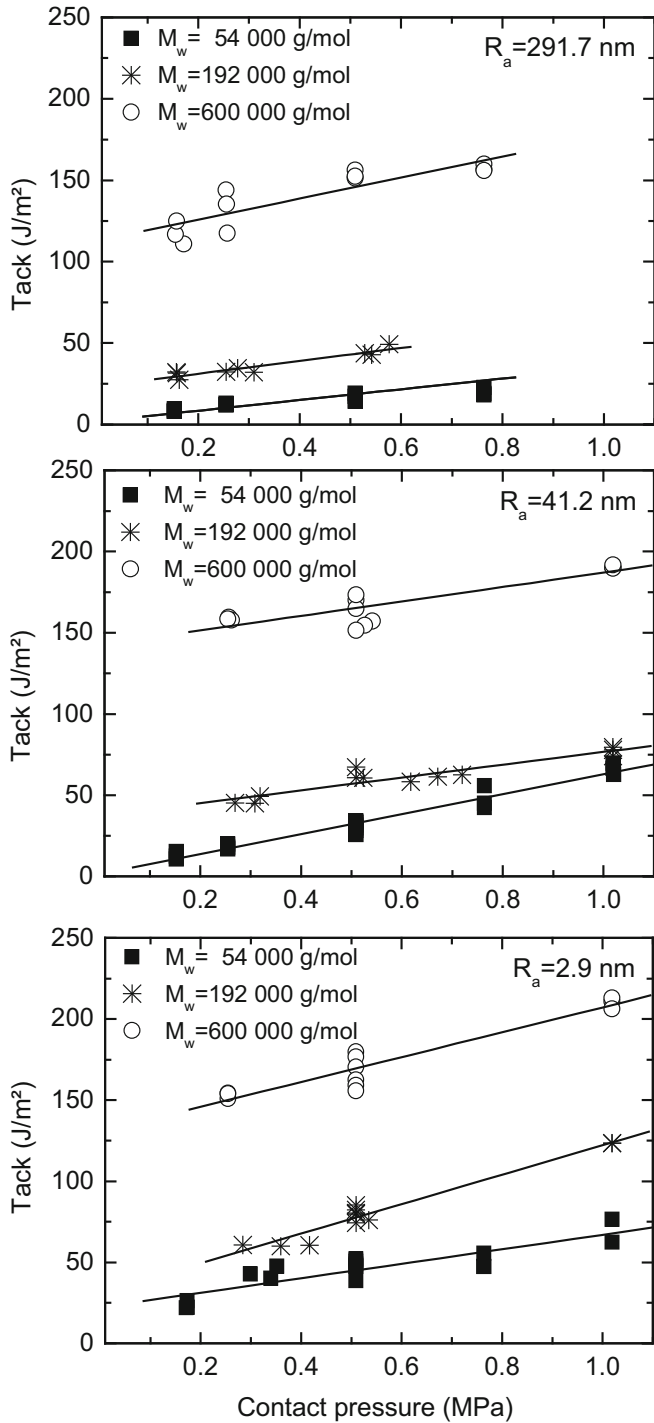


Fig. 6. Tack vs. contact pressure for BA/MA PSAs of three molecular weights, measured using the probes of three different average surface roughness. Lines are to guide the eye.

Fig. 7. Representative nominal stress–strain curves for BA/MA PSAs of three molecular weights, measured using the probes of three different average surface roughness.

strongly decreases with increase in roughness, and it appears earlier for the higher R_a values. This result is in agreement with an earlier study [12] and can be rationalized in terms of an inhomogeneous stress distribution at the interface. Local stresses may be higher than the average nominal stress at the nucleation sites on a rough surface. From stress–strain curves one can also see that after the maximum is reached, the nominal stress decreased in all cases with similar speed. However, in a previous study [12] it was shown that the nominal stress after the maximum decreased distinctly faster when the smooth probe was

used than in the tests with the rough probe, thus causing the stress–strain curves to cross. This characteristic difference in the debonding behavior may presumably be related to the fact that crosslinked acrylic PSAs were used in this work, whereas a styrene–isoprene–styrene triblock copolymer and a hydrogenated resin were used in [14]. These distinctly different findings indicate that the cavitation process seems to be controlled by a delicate interplay between polymer composition and probe roughness. The deformation at break is independent of roughness, but increases strongly with increase in molecular weight of the PSA

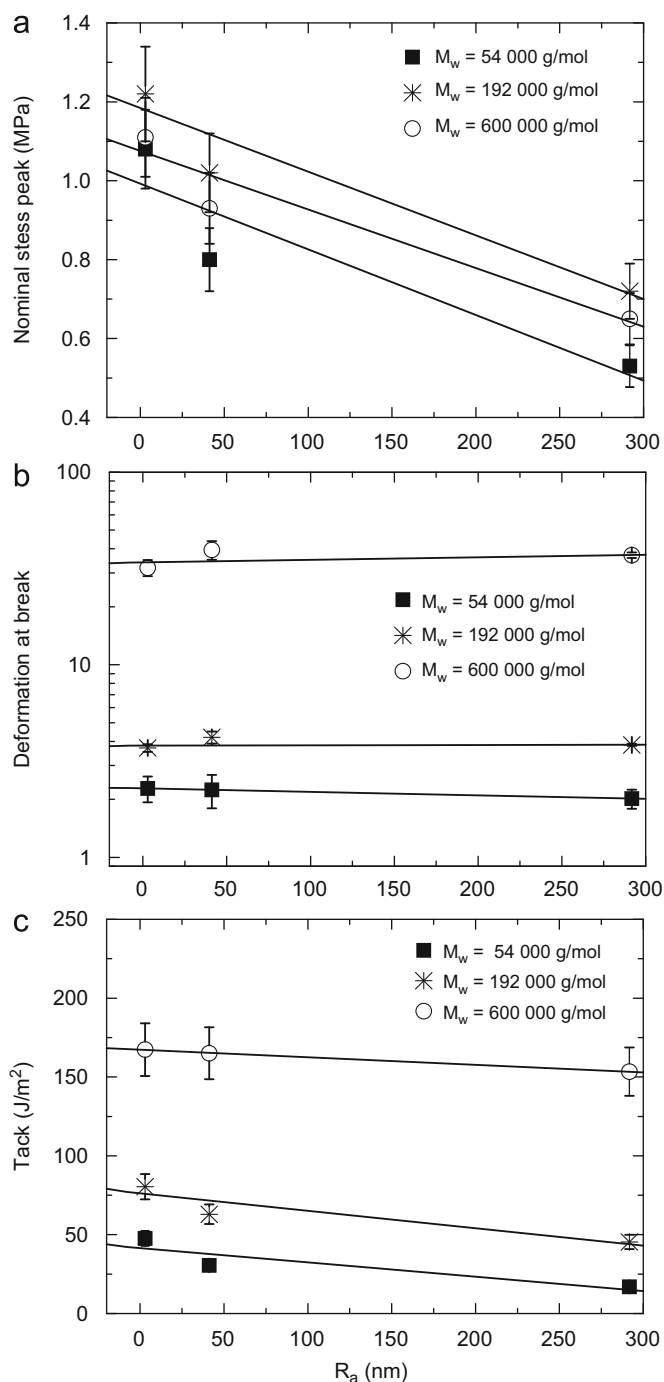


Fig. 8. Nominal stress peak (a), deformation at break (b) and tack (c) vs. average surface roughness (R_a) of the probes for BA/MA PSAs of three molecular weights. Lines are to guide the eye.

used (Fig. 8b). This result can be explained as follows: the final plateau in nominal stress corresponds to vertical growth of cavities or stretching of the formed fibrils. The ability of the fibrils to be deformed (fibril stability) is mainly controlled by the viscoelastic properties of the polymer material and surface roughness plays no role. Finally, the tack decreases with increase in roughness according to the contribution of the nominal stress peak (Fig. 8c). This decrease is only weak, since the tack value is dominated by the formation and elongation of fibrils and this process mostly depends on the viscoelastic properties of the PSA. Within the range of molecular weights investigated here, the PSA with the highest molecular weight

exhibits the highest tackiness due to the strong contribution of filament stretching. This corresponds to the strong increase of the moduli G' and G'' with molecular weight (see Fig. 5) in the frequency range corresponding to the characteristic debonding rate in our tack experiments ($\approx 1 \text{ s}^{-1}$). The shear moduli in this frequency range and accordingly the tack are expected to level off at higher molecular weight as shown in [6].

3.3. Video-optical observation

To investigate the process of debonding in detail and to evaluate the effect of surface roughness on cavitation, we have recorded images of the contact area of the probe with the PSA film simultaneously with tack curves. Fig. 9 shows the representative images of cavities present at the moment, when their lateral growth is finished. From the obtained images one can see that cavities that appear on the smooth surface are bigger and less circular than those on the rough one. Additionally, the cavities formed on the smoother surface have a finger-like shape as already reported in [12]. The total number of cavities and the average final cavity area were calculated from the images in Fig. 9 and are shown in Fig. 10 as functions of the average probe roughness. Surface roughness has a significant effect on the number of cavities and on their size. The number of cavities increases with increase in roughness, a fivefold increase of the average total number of cavities formed is observed, when increasing the surface roughness from 2.9 to 291.7 nm (Fig. 10a). The stronger cavitation on the rough surface is the result of a larger amount of contact defects, which act as germs for cavity formation. Accordingly, the average final size, which cavities can reach, reduces (Fig. 10b), and in addition the cavity size distribution is much broader than that in the smooth surface. Nevertheless, the viscoelastic properties of PSAs have a comparable impact on the cavitation process. An increase of the molecular weight of the PSA from 54 000 to 600 000 g/mol results in an average increase of the total number of cavities by a factor of 6 (Fig. 10a). Thus, in addition to the influence of contact defects, viscoelastic properties play an important role in cavity formation, too. From Fig. 10b one can see that the final average cavity area

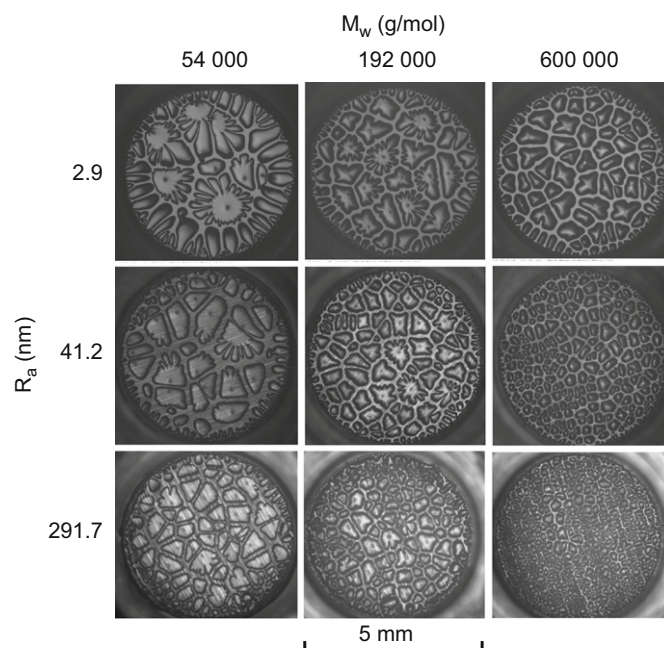


Fig. 9. Representative images of contact area of the probes with three different average surface roughness for BA/MA PSAs of three molecular weights.

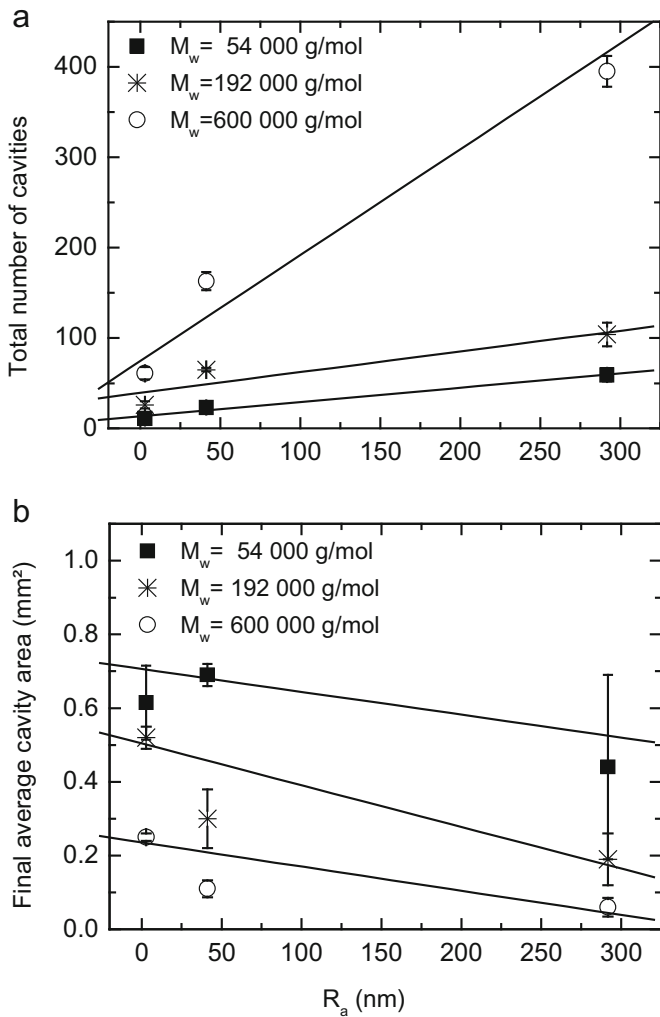


Fig. 10. Total number of cavities (a) and final average cavity area (b) vs. average surface roughness (R_a) of the probes measured for BA/MA PSAs of three molecular weights. Lines are to guide the eye.

only slightly decreases with increase in roughness, while the effect of molecular weight is much more pronounced. The higher the molecular weight (for the same roughness), the higher the viscosity, and the worse should be the wetting at the interface. As a result the number of cavities increases and their final size decreases.

In a previous study [14] the effect of surface roughness of both probe and adhesive films on the cavitation process was studied. The cases of smooth and rough adhesive films, both tested with a smooth probe ($R_a = 10$ nm), were analyzed in detail. It was claimed that in this case the size of the cavities and their areal density is insensitive to the interface, because cavities grow in the bulk of the polymer film and their size is controlled by the elastic properties of the material used. Here we would like to emphasize that from our results shown in Fig. 10 one can clearly see that although viscoelastic properties of PSAs play a decisive role, the number of cavities and their area are very sensitive to the roughness of the probe used.

Video sequences were analyzed quantitatively and the number and size of individual cavities were determined depending on time to study the kinetics of cavity growth. Fig. 11a shows the number of cavities as a function of time with synchronized stress vs. time curves for the PSA with $M_w = 600\,000$ g/mol measured with probes of three different roughnesses (similar results were

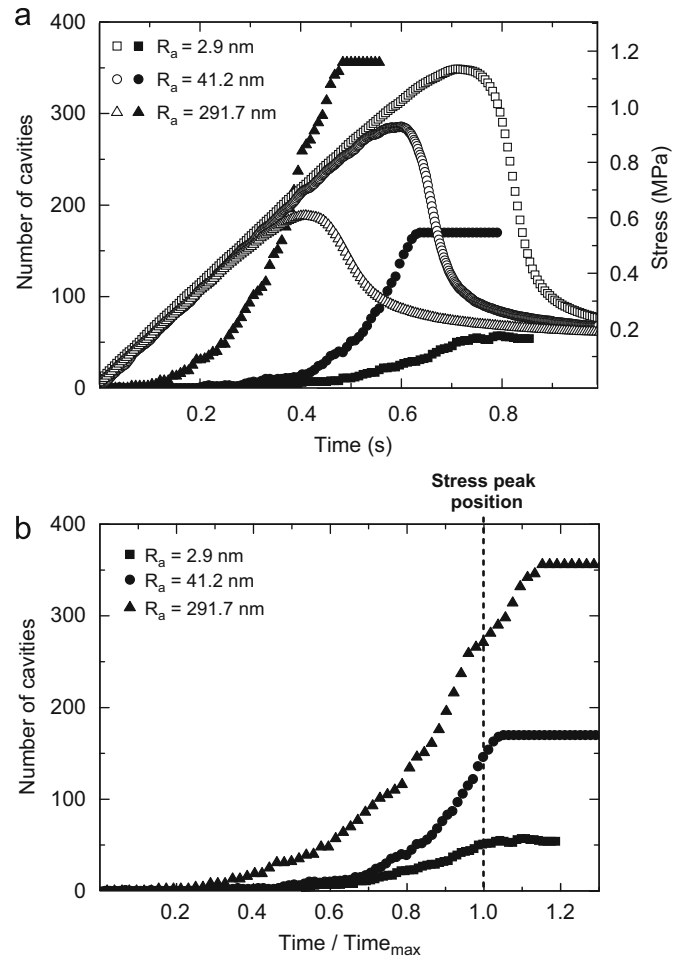


Fig. 11. Number of cavities (closed symbols) and stress (open symbols) as a function of time (a) and number of cavities vs. time/ time_{max} (b) for BA/MA PSA with $M_w = 600\,000$ g/mol measured with probes of three different roughness.

obtained for polymers with other M_w). The first thing to be noticed is that the formation of the first cavities starts already long before the stress reaches the maximum value. The number of cavities increases slowly at the beginning of debonding and then grows rapidly as the stress peak is approached. In Fig 11b we plot the number of cavities as a function of time divided by the time where the stress peak is reached. On the rough surface, additional cavities appear even after the stress peak has been passed. Nevertheless, in all cases most of the cavities appear in the time interval when the stress peak is approached, but emergence of new cavities ceases before the stress starts to decay significantly and eventually reaches the characteristic plateau value.

Fig. 12 shows an example of a stress vs. time curve and corresponding equivalent cavity radius vs. time curves. Additionally, images are shown, corresponding to the times marked with vertical dashed lines on the curves. These measurements were performed on a PSA with $M_w = 54\,000$ g/mol using the probe of $R_a = 41.2$ nm. Time zero on both graphs corresponds to the zero crossing of the force measurement. From the series of typical curves of cavity radius vs. time one can see that cavity growth continues almost until the characteristic plateau of the stress curve is reached. Furthermore, one can distinguish two types of cavities. The cavities of the first type (filled symbols) appear at the very beginning, long before the stress approaches its maximum. These cavities grow slowly from the beginning of debonding and then increase their growth rate when the stress peak is approached. A similar behavior has been

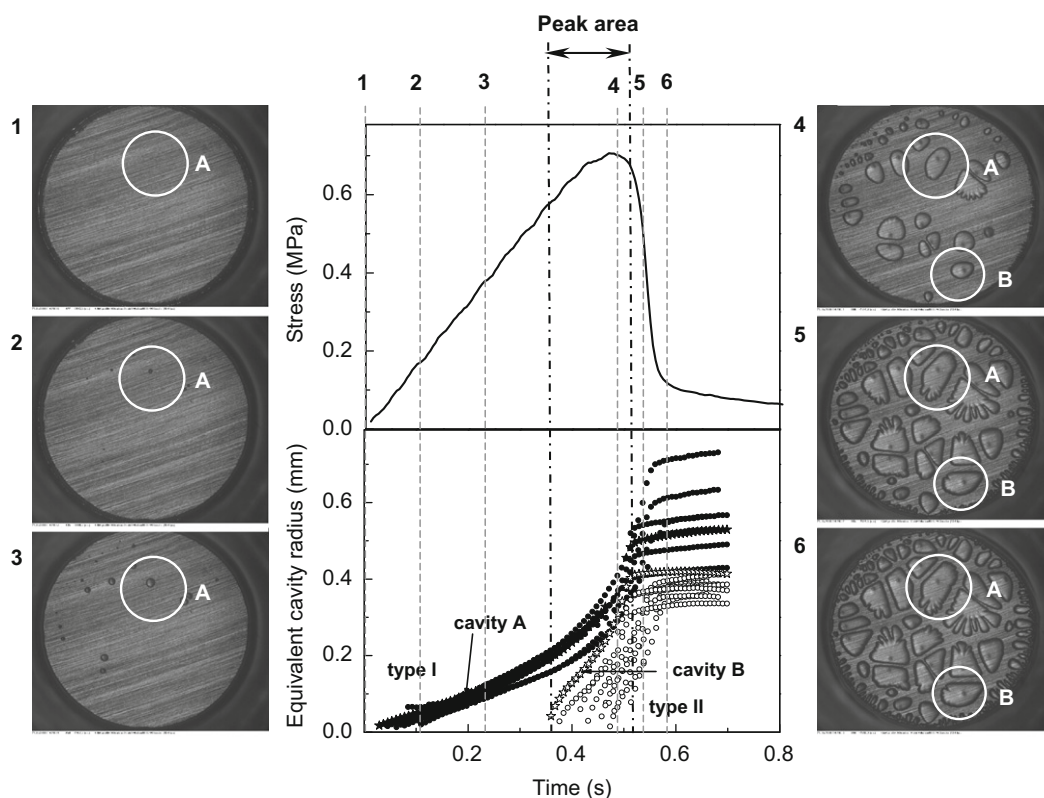


Fig. 12. Typical stress vs. time curve and corresponding equivalent cavity radius vs. time data measured using the probe of average surface roughness $R_a=41.2$ nm on the BA/MA PSA of $M_w=54\,000$ g/mol. In addition a sequence of images is shown illustrating the occurrence and growth of cavities of type I (A) and type II (B).

reported in [13]. But in contrast to the exponential increase in cavity size observed there, the increase in growth rate observed here is much less pronounced. The cavities of the second type (open symbols) appear later, in the area of the stress peak, and grow rapidly with a constant speed.

Cavity growth rate was also discussed in [14]. However, it was claimed there, that on the rough interface all cavities expand simultaneously from contact defects, grow at the same rate and have a similar size at any given time. On the smooth interface cavities occur sequentially and their growth rate increases with stress level, at which they appear. Cavities grow the more rapidly, the later they start to grow, i.e. the higher the applied stress. In contrast, our experiments suggest that for all probe roughnesses studied there are always two types of cavities, those appearing early and growing slowly, and those appearing later growing with a higher rate.

Fig 13 shows the cavity growth rate as a function of the average roughness of the probe for both types of cavities. Cavities of the second type grow approximately five times faster than the ones of the first type. One can also see that the surface roughness has practically no influence on the cavity growth rate for both types of cavities. In contrast, it was speculated in [12], that a rough surface slows down the growth of cavities. The authors observed that the slope of the stress vs. strain curves just after the maximum stress decreased with increase in roughness and this was interpreted as decrease of the lateral propagation rate of cavities. However, our experiments show that for BA/MA PSAs the slope of representative stress vs. strain curves is essentially independent of surface roughness (Fig. 7) and no influence of roughness on the cavities growth rate is seen (Fig. 13). Moreover, the growth rate significantly decreases with increase in molecular weight of the polymer. This demonstrates that, although surface roughness defects play a significant role in the cavitation process,

the cavity growth rate is determined by the viscoelastic properties of the PSAs. Cavities appear at the surface defects, but they grow into the bulk polymer material; therefore their growth rate is insensitive to surface roughness.

4. Concluding remarks

The effect of surface roughness on the adhesion behavior of uncrosslinked BA/MA PSAs has been investigated using the probe tack test combined with video-optical imaging of the cavitation process. It was found that an increase in probe surface roughness leads to a drop of the stress peak value. On the other hand, the plateau of the stress curve and the deformation at break are found to be independent of roughness and increase strongly with increase in molecular weight of the PSA. This is expected since these parameters correspond to the vertical growth of the fibrils, which is mainly controlled by the viscoelastic properties of the PSA. The tack value or the work of adhesion decreases with increase in roughness according to the contribution of the stress peak, but the impact of surface roughness on tack decreases with increase in M_w , since the contribution of the plateau region of the stress-strain curve becomes more and more dominant.

Nevertheless, a detailed video-optical investigation of the cavitation process shows that surface roughness plays a significant role in the formation and growth of cavities. The total number of cavities formed grows and their size decreases with increase in roughness.

The number of cavities increases slowly with time at the beginning of debonding, and then rapidly increases as the stress peak is approached. The final number of cavities is reached later on the rough surface than on the smooth one; on the rough surface additional cavities appear even after the stress peak has

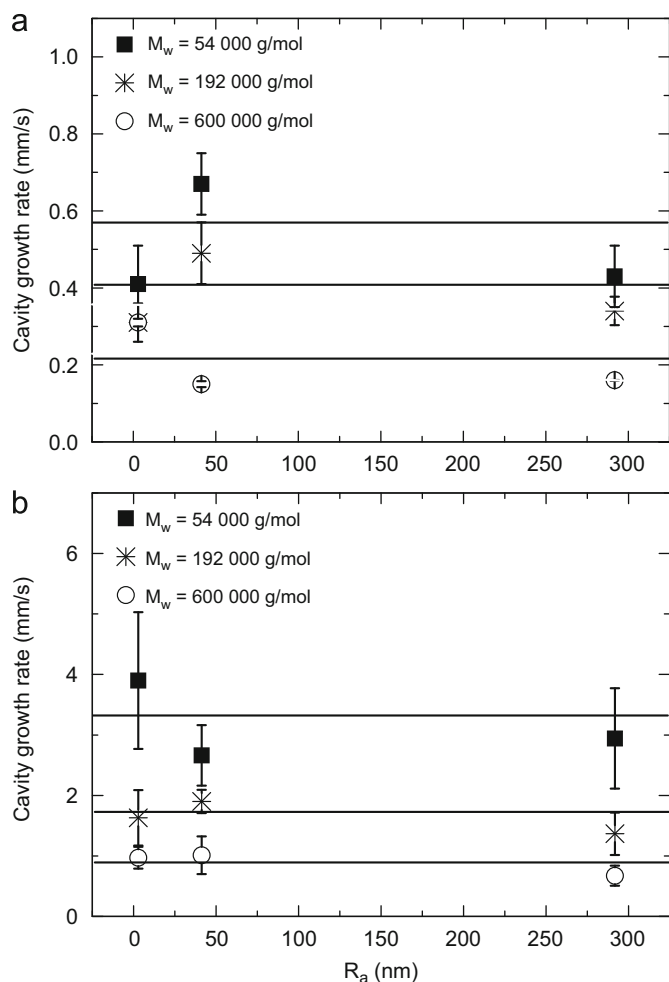


Fig. 13. Cavity growth rate vs. average surface roughness (R_a) of the probes measured for BA/MA PSAs of three molecular weights: (a) type I cavities occurring at the beginning of debonding; (b) type II cavities occurring in the area of the stress peak. Horizontal lines are to guide the eye.

been passed, but not during the period where the nominal stress drops to its plateau value. There are always two types of cavities formed during the debonding process. Cavities of the first type appear at the beginning of debonding and initially grow slowly. Cavities of the second type appear at a higher stress level close to the stress peak and their growth rate is about five times higher. Cavity growth stops when the plateau of the nominal stress is reached. For both types of cavities the growth rate is found to be insensitive to surface roughness, but strongly decreases with increase in polymer molecular weight, i.e. the phenomenon of cavity growth is also strongly controlled by viscoelastic PSA properties.

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