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SURFACE AND ADHESION PROPERTIES OF URETHANE ACRYLATE GRAFT COPOLYMERS

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Abstract: A solvent –based adhesive in which a continuous phase includes a solvent for an acrylic based adhesive or a solvent for a urethane based adhesive and wherein adhesive molecules and dissolved in the solvent to form said continuous phase, the adhesive being characterised in that adhesive molecules include graft polymer where in a major part of the molecule is either acrylic based or urethane based such that the major part is of sufficient size to provide the adhesive molecule with a required solubility in said solvent and wherein a minor part of the molecule is based on the other of said acrylic or urethane thereby providing said molecule with attributes of both acrylic based and urethane based adhesives. Adhesion increased as the content of urethane macromonomers (UMs) increased in graft copolymer. The graft copolymer prepared using a high UM feed for both PMMA and PnBMA showed improved in adhesion compared to the pure methacrylate polymers. The adhesion was better whether for leather and for vinyl. Surface and adhesive properties were improved as the amount of UM content increased in the graft copolymer. Smaller contact angles result giving a surface with a higher surface energy and increase in T-peel strength was observed as the amount of UM content increased in the graft copolymer.

Key words: polyurethane – graftcopolymer- acrylic polymer –surface properties- adhesion.

I. INTRODUCTION

Adhesion is the intermolecular action at the interface of two surfaces.¹ It's a multi-disciplinary topic which includes surface chemistry, physics, rheology, polymer chemistry, stress analysis polymer physics and fracture analysis. Describing the mechanism of adhesion in simple terms is difficult due to the complexity and evolving understanding of the subject. A range of adhesion mechanisms are based variously on diffusion, mechanical, molecular and chemical and thermodynamic adhesion phenomena.²⁻⁵

Applications for polyacrylate homopolymers and polyurethanes have shown remarkable growth over the last

years. Many industrial applications require good adhesion properties and it is known that in general purpose adhesives, the favourites are: the monomeric acrylates, such as super glue, which cure from monomer to polymer, the acrylics in solvent,⁶ polyurethane in solvent^{7,8} or a moisture curing grade of polyurethane; two part epoxy resins^{9,10} and finally emulsion based polyvinyl acetates,¹¹ commonly known as wood glue.¹²

The major market however, is solvent based and is dominated by acrylic using a low temperature solvent such as a MEK solvent mixture. PUs requires a higher boiling solvent, which can be as exotic as n-Methyl-2-pyrrolidone (NMP) where the solvent is mostly evaporated, the urethane heated and the two surfaces joined. This is a difficult high-tech glue to use, not generally accepted for household use.

In this study a graft, copolymer has the properties of both an acrylic and a urethane and then to increase the solubility of the urethane in a common solvent by it being pulled into solution by the acrylic part of the molecule. As the solvent evaporates two phases form and either phase can be continuous, but it is preferential for price to have a continuous acrylic phase with nano inclusions of polyurethane, which means that either the acrylic or the urethane phase can associate with the surface to be glued. This we have proved previously in rolled steel research by mixing three urethanes with different functionality and finding enrichment of the correct one at the adhesive surface phase and enrichment of the correct one at the air surface phase and modulus improvement of the entire adhesive film by enrichment of the high modulus component in between these.¹³ This has also been proven in early polycarbonate bullet proof transparent sheets, where the soft silicone rubber required needed to be soft, but bond securely to the polycarbonate.¹⁴ Here block polymers of polycarbonate with silicone were used with excellent bullet stopping effects, no easy delamination.

II. THEORETICAL AND BACKGROUND

For any material, the molecules in the bulk have no net force acting on them, while the ones at the surface encounter a net force inward. For solids, this force is called as "surface free

energy" (SFE) or surface tension and defined as the amount of energy required to change the surface area of a material by one meter square. Knowing the SFE value of a material, one can predict whether the material is wettable or not by a certain liquid. Solids, which have the similar or higher SFE than that of a liquid's SFE are wettable by that liquid.¹⁵ Contact angle (θ) of a liquid drop is the angle formed by the surface and the tangent of the drop at the point it touches to the surface. Contact angle indicates the strength of non covalent forces between the liquid and the first monolayer of the material. The liquid drop spreads on the solid and wets the surface, in case of strong interactions between phases.¹⁶ Zero contact angles mean a strong interaction between the phases and complete wetting by the liquids. SFE can be obtained by using different approaches.¹⁷ All these methods are based on contact angle measurements, but they may have discrepancies in the results.^{15,17} In this study the harmonic mean approaches was used to measure the surface tension of UM and its graft copolymers.

In the harmonic mean approaches The surface tension of polymer can be divided into a non-polar dispersion component, γ^d and the polar component, γ^p that is $\gamma = \gamma^d + \gamma^p$

The harmonic mean is Eq (1)

$$(1 + \cos\theta_i) \gamma_i = 4 \left[\frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right] \quad (1)$$

If the subscript 1 expresses water, the surface tension, dispersion component, and polar components of water are:

$\gamma_1 = 72.8$, $\gamma_1^d = 22.1$, $\gamma_1^p = 50.7$. If the subscript 2 expresses glycerol, the surface tension, dispersion component, and polar component of glycerol are: $\gamma_2 = 64$, $\gamma_2^d = 34$, $\gamma_2^p = 30$.

According to the above mentioned parameters and the contact angle θ_i of water on the surface of polymer and glycerol on the surface of polymer as well as the harmonic mean Eq. (1), two simultaneous equations can be obtained, one from the polymer and water, the other from the polymer and glycerol. The dispersion component γ_s^d and polar component γ_s^p of each polymer can be gained by solving the two simultaneous equations.

Contact angle (θ_i) for a sessile drop, is defined by the tangent at the air /liquid/ solid line of contact and line of contact and line through the base of liquid drop where it contacts the solid.¹⁸ Each contact angle was calculated by the following equation:

$$\text{Contact angle } (\theta) = 2 \times \tan^{-1}(h/r) \quad (2)$$

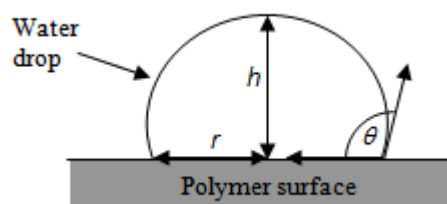


Figure 1: Image of a water drop showing the height and radius used in determination of the contact angle θ .

III. EXPERIMENTAL

Materials

Any consideration of adhesion mechanisms requires information about the physical and chemical properties of the adhering surfaces and the delamination surfaces in cases where adhesion has failed in use or as a result of mechanical testing. Urethane macromonomers (UM1 and UM2) and all their graft copolymers (PMMA-g-UM and PnBMA-g-UM2) were described previously.¹⁹ Glycerol ($\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$) was product of Merck. Deionized water (DDI, from a Millipore milli-Q purification system) and silicon oil (SA Silicones)

Optical contact measurement

Sample films were prepared by melt pressing at temperatures between 40 and 200 °C. A 1 μl drop of water or glycerol was placed onto the sample film and the magnified image was captured using a Nikon SMZ-2T (Japan), model VCC 25°C digital video camera. Figure1 shows a cartoon of a captured image. Included on the image are the parameters used to determine the static contact angle according to the relationship in Equation 1 below. PVR-plus software was used for imaging along with an Able Image analyzer (μ -labs) version V3.6, which enabled determination of the lengths associated with contact angle calculation. For the statistical approach, at least five (mostly 8) values were measured for each liquid. Drops which had unsymmetrical forms (difference between the angles at both sides being higher than 5°) were excluded. The temperature of the environment was fixed at 20°C. The contact angle results are given in Table 1.

Surface energy measurement

The surface energy of urethane macromonomers and methacrylic /urethane graft copolymer was determined via measurements of contact angles of a set of testing liquids (i.e. re-distilled water, glycerol). The drop of the testing liquid ($V = 1 \mu\text{l}$) was placed on the polymer surface, and a contact angle of the testing liquid was measured. The surface energies of the polymer were evaluated by harmonic mean equation. In the calculations two simultaneous equations can be obtained, one from the polymer and water,



the other from the polymer and glycerol and Windows Excel program were used.

Adhesive preparation

The samples were prepared by dissolving PMMA, PnBMA, and their graft copolymers which have high percentages of UM2 content (UM1 copolymer only dissolved in a strong solvent like NMP i.e. MEK was/is not a good solvent for this adhesive) into a solvent comprising 50 wt % THF 25 wt % acetone and 25 wt % ethanol and the solid content of the sample was 35 wt %.

Peel test

The substrates used for peel tests i.e. commercial leather or vinyl were cut and the dimensions of the substrates were 8 cm × 2 cm for the T- peel test. However, the adhesive coating area was 6 cm long. The sample of copolymer/solvent glue was then placed on the commercial leather or vinyl to form the testing sample which was conditioned at room temperature using a pressure of a 5 Kg weight on the test piece.

A T-peel test was carried out using a Universal Testing Machine (UTM) (LLOYD Instruments-Model LRX 5) at a rate of 50 mm/min at room temperature, the Scotch tape of width 2.5 cm was stuck over a length of 4.0 cm on the sample polymer film. Care was taken to see that there were no air gaps or wrinkles and was kept under a pressure of 1.0 kg for 10 min. The T-peel test was carried out after fixing one end of the sample in one jaw and the Scotch tape end with other piece of sample adhered to it in the other jaw. T-peel strengths are reported as force of peel per millimeter of sample width. For more accuracy the T-peel test was repeated 5 times for each sample and the average T-peel strength was recorded. Table 3 shows calculation of peel strength of commercial vinyl and leather for the two synthesized graft copolymers containing different amounts of UM2.

IV. RESULTS AND DISCUSSION

Optical contact angle analysis (OCA) is a surface sensitive technique which allows the surface energy of the investigated sample to be measured. The contact angle results are given in Table 1. In general, a polar and non-polar liquid are dispensed onto the sample surface with the angle that the liquid makes with the surface (as measured through the liquid) being recorded. Smaller contact angles indicate a more wetting surface with a higher surface energy and therefore a greater work of adhesion.²⁰ As surface energy and wettability are related to adhesion, OCA provides an indirect measure of adhesion, allowing for the comparison between the work of adhesion and direct adhesion methods. The contact angle results are given in Table 1

Figure 2 (a to d) shows the contact angles of re-distilled water deposited on the surface of graft copolymer surface films vs UMs content. The contact angles of water in Figure 2 (a) to (d) decreased by increasing the amount of UM which was incorporated into the PMMA or PnBMA backbones. The contact angles of PMMA-g-UM1 copolymers decrease from 96.19° for only PMMA, to 72.91° for 40.4 wt % of UM1 in the graft copolymer and the contact angle of PnBMA-g-UM1 copolymers decrease from 95.13° for only PnBMA, to 75.02° for 42.55 wt % of UM1 in the graft copolymer. On other hand the contact angles of PMMA-g-UM2 copolymers decrease from 96.19° for only PMMA, to 79.46° for 36.50 wt % of UM2 in the graft copolymer and the contact angle of PnBMA-g-UM1 copolymers decrease from 95.1° for only PnBMA, to 78.84° for 38.00 wt % of UM2 in the graft copolymer. Since the surface energy of PMMA and PnBMA lower than the surface energy of UM1 and UM2; the PMMA or PnBMA segments migrate away from the top of the surface to leave a hydrophilic-enriched layer that can interact with the water. Micro-phase separation in graft copolymers occurs even at relatively low UMs content due to dissimilarity between the chemical structures of the PMMA or PnBMA,

Table 1: Contact angle values of synthesized polymer

Sample code	UM% (wt %)*	Contact angle (θ_1) H ₂ O
UM1	100	74.2
PMMA	0	96.2
G10M1 (PMMA-g-UM1, 10 wt % UM1 feed ratio)	4.3	91.2
G25M1	19.2	83.5
G55M1	40.4	72.9
PnBMA	0.0	95.1
G10B1 (PnBMA-g-UM1, 10 wt % UM1 feed ratio)	4.2	89.1
G25B1	18.8	81.3
G55B1	42.6	75.0
UM2	100	75.1



PMMA	0	96.2
G10M2 (PMMA-g-UM2, 10 wt % UM2 feed ratio)	3.1	90.1
G25M2	20.4	85.2
G55M2	36.5	79.5
PnBMA	0	95.1
G10B2 (PnBMA-g-UM1, 10 wt % UM2 feed ratio)	6.2	90.1
G25B2	17.0	87.6
G55B2	38.0	78.8

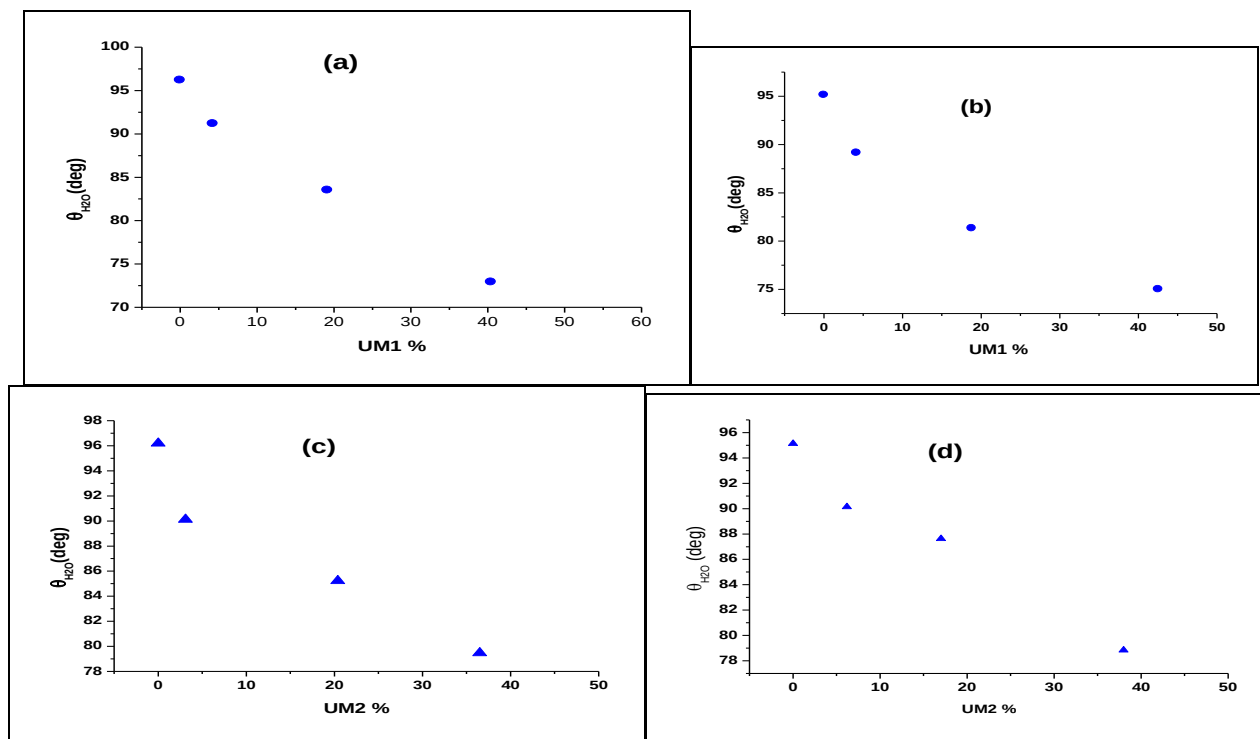


Figure 2: Contact angles of water vs the content of urethane macromonomer in graft copolymerization (a) Contact angles of water vs. UM1/MMA content (b) Contact angles of water vs. UM1/n-BMA content (c) Contact angles of water vs. UM2/MMA feed ratio (d) Contact angles of water vs. UM2/n-BMA content.

The dependencies of the surface energy and its polar component on the graft copolymers were determined by the harmonic mean method vs. the content of the UMs incorporated in the graft copolymer are shown in Table 2.

This table lists the surface tensions of each polymer measured by contact angle method, where the subscript 1 expresses water, the subscript 2 expresses glycerol.

Table 2: Contact angles and surface tensions for synthesized polymer

Sample code	θ_1	θ_2	γ_s^a	γ_s^p	γ_s (mN.m ⁻¹)
UM1	74.2	62.2	26.1	9.8	35.9
PMMA	96.19	84.5	20.7	2.4	23.1
PnBMA	95.13	83.2	21.6	2.5	24.1
G55M1	72.91	73.4	4.9	26.5	31.4
G55B1	75.02	74.5	5.8	23.4	29.2
UM2	75.13	67.2	21.7	11.2	32.9
G55M2	79.46	75.9	9.1	25.5	25.5
G55B2	78.84	78.7	4.8	21.6	26.4



Table 2 shows that, the surface energy of all synthesized graft copolymer increase significantly with the concentration of UMs. The surface energy of PMMA-g-UM1 copolymers increases from 23.14 mN.m^{-1} for only PMMA, to 31.42 mN.m^{-1} for 40.44 wt % of UM1 in the graft copolymer and the surface energy of PnBMA-g-UM1 copolymers increases from 24.07 mN.m^{-1} for only PnBMA, to 29.23 for 42.55 wt % of UM1 in the graft copolymer. On other hand the surface energy of PMMA-g-UM2 copolymers increase from 23.14 mN.m^{-1} for only PMMA, to 25.52 mN.m^{-1} for 36.50 wt % of UM2 in the graft copolymer and the surface energy of PnBMA-g-UM2 copolymers increase from 24.07 mN.m^{-1} for only PnBMA, to 26.43 mN.m^{-1} for 38.0 wt % of UM2 in the graft copolymer. This indicates that the phase separated phases need much longer relaxation times for the urethane component to play a decisive role by rising to the surface.

In addition, the increase in the polar and decrease in the dispersive forces of surface energy in much the same order, is much more remarkable. It says that the surfaces become more hydrophilic with increasing polar share as expected, i.e. the contact angle of water drops falls due to the better wetting (as the UM content into graft copolymer increases). High energy values are favorable for wetting a surface. Polar interactions due to dipoles also have much higher bonding energies than dispersion forces; so that one can also expect high polar energy contributions to lead to a good adhesion. In other words smaller contact angles indicate a more wetting surface with a higher surface energy and therefore a greater work of adhesion.

Figure 3 shows the dependence of the T-peel strength of the adhesive joint of the methacrylate/urethane graft copolymer vs. content of UM2 using commercial vinyl or leather as substance in the T-peel test. It is seen that the peel strength of the adhesive joint of the methacrylate/urethane graft copolymer increases with growth in UM2 content in the

whole concentration range. The facts that peel strength of the adhesive joints increases with increase in UM2 content reflect the modulus increase of the adhesion. Figure 3. (a) shows the dependence of the peel strength of adhesive joint PMMA/UM2 graft copolymer vs. content of UM2 using commercial vinyl or leather as substance in the T-peel test. A maximum value is observed for the PMMA/UM2 graft copolymer at 36.5 wt % of UM2 in both leather and vinyl. Comparing PMMA with PMMA-g-UM2 copolymer containing 36.5% of UM2 shows that the peel strength of the adhesive joint to commercial vinyl or leather increased 1.4 and 1.9 times respectively. The increase of peel strength to the maximum value is attributed to the modulus increase as well as the increasing wettability of the adhesive which enhances the peel adhesion property of the adhesive. The final increase in the UM2 content decreases the compatibility of copolymer parts of PMMA and UM2 as reflected by the higher peel strength. Similar observation is also obtained for PnBMA/UM2 graft copolymer. Figure 3 (b) shows the dependence of the peel strength of the adhesive joint of the PnBMA/UM2 graft copolymer vs. content of UM2 using commercial vinyl or leather as substance in T-peel test. Comparing PnBMA homopolymer with PnBMA-g-UM2 copolymer containing Figure.0% of UM2 shows that the peel strength of adhesive joint to commercial vinyl or leather increased 1.2 and 1.2 times respectively. This increase in the peel strength is due to increasing wettability of the adhesive which enhances the peel adhesion property of the adhesive. All the peel strength results for all the synthesized PnB-methacrylate/UM2 graft copolymers and which contain different amounts of UM2 are shown in Table 3. The main increase is probably because of the modulus (stiffness) increase as the UM2 content increases.

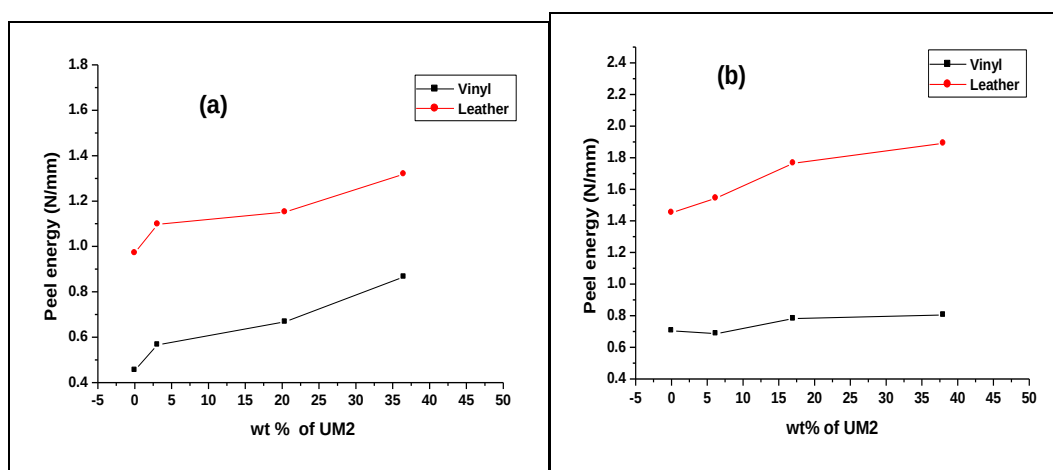


Figure 3: Peel strength of (a) PMMA-g-UM2 (b) PnBMA-g-UM2 versus UM2 content.



Table 3: Peel energy of commercial vinyl and leather for synthesized graft copolymer containing different amount from UM2.

	Sample code	UM2 incorporated into copolymers as calculated by ¹ HNMR (wt %)	Force (N) (vinyl)	width	Peel energy (N/MM)	Force (N) (Leather)	width (MM)	Peel energy (N/MM)
PMMA-g-UM2	PMMA	-	4.545	20.2	0.455	10.39	21.4	0.971
	G10M	3.1	5.87	20.7	0.567	11.09	20.2	1.098
	G25M	20.4	7.23	21.0	0.668	11.98	20.8	1.151
	G55M	36.5	9.576	22.1	0.866	13.33	20.1	1.319
PnBMA-g-UM2	PnBMA	-	6.95	19.7	0.705	14.34	19.7	1.452
	G10B	6.2	7.32	21.3	0.687	15.82	20.5	1.543
	1025B	17.0	7.85	20.1	0.781	16.91	20.2	1.764
	G55B	38.0	9.13	22.8	0.805	19.58	20.7	1.891

V. CONCLUSIONS

The surface, modulus (stiffness) and the adhesive properties improved as the amount of the UM incorporated in the methacrylate/ urethane graft copolymer increased.

(a) Values of the contact angles of the water decreased by increasing the urethane macromonomer content in the methacrylate/urethane graft copolymer i.e. wets easier, more hydrophilic and stiffer.

(b) Surface tension increased by increasing the urethane macromonomer content in methacrylate/ urethane graft copolymer.

(c) A maximum value of peel strength is also observed with the maximum UM2 content in the methacrylate/urethane graft copolymer.

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