High function pressure sensitive adhesives

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A pressure sensitive adhesive (PSA) is a type of adhesive that can bind the materials together immediately and be removed when necessary. Due to its convenience, it is widely used in various applications and fields including packaging, electronics, optics, automobiles, building materials, and medical care. Highly functional PSAs are demanded especially in the fields of electronics, optics, and medical care, and removability to allow the user to peel smoothly with a light force, and stability of the PSA properties are some of the important functions. This article introduces 'POLYTHIC UP' Series, which consists of urethane PSAs that are being developed to meet these needs.

Physical properties required in a PSA

In order for the PSA to adhere to an object, it needs to have the adhesive property when it touches the object called "tack" (tackiness) as well as the "adhesive force" appropriate for the purpose. To maintain adhesion, it is also required to maintain "shear adhesion," which allows the adhesive to retain the adhering state and withstand shear. On the other hand, it needs to have the function to be removed cleanly (removability). Such seemingly conflicting functions can be achieved when the PSA is a viscoelastic body. PSA properties are related to the dynamic viscoelastic behavior, and it is desired that the storage modulus (G') of the PSA is larger in order to increase the adhesive force and shear adhesion. However, if the elastic modulus is too large, the material becomes too hard to be a PSA, which reduces the contribution of viscosity and causes the tackiness at the interface with the adherend to become insufficient. This, therefore, means that there are optimal values in shear adhesion and elastic modulus. Furthermore, it is better that the PSA has a higher cohesive force if the removability is considered more important, and its composition is designed so that it exhibits the PSA properties suited to the purpose in order to ensure that separation occurs only at the interface between the PSA and the adherend with no residual adhesive or damage on the adherend.
Especially in electronic, electrical and optical applications and medical applications, PSA properties are controlled precisely so that it does not cause adverse effects on the delicate parts and materials or the tissues such as skin. Problems such as failure to give the proper performance as adhesives, causing damage to the adherend and residual adhesive on the adherend may occur at separation if the intended PSA properties happen to vary due to external factors such as time, temperature, and peeling rate. Therefore, not only the intended PSA properties, low dependency on external factors are important[1].

Types of PSAs and the characteristics of each

In general, the types of PSAs include acrylic-based, rubber-based, silicone-based, and urethane-based. While acrylic- and rubber-based PSAs are most widely used as they have wide design ranges from slightly adhesive to highly adhesive and are relatively inexpensive, they also have high dependency on external factors such as time, temperature, and peeling rate. On the other hand, silicone- and urethane-based ones have relatively lower dependency on these factors, and deliver a stable adhesive force in a wide range of environments. However, silicone-based PSAs are expensive, and have some disadvantages, including low-molecular-weight silicone components migrating to the adherend and causing contamination.
Meanwhile, urethane-based PSAs deliver strength in slightly adhesive applications where removability is considered especially important, as they have excellent oil resistance and abrasion resistance, as well as favorable features including high adherend wetting property and adhesion to the adherend, high moisture permeability, and being easy to give antistatic properties thanks to the high polarity of the urethane group, in addition to the low dependency on time, temperature, peeling rate and so forth.
Fig. 1 shows the dependency of viscoelasticity of acrylic-based and urethane-based PSAs on the temperature by dynamic viscoelasticity measurements. The acrylic-based PSA becomes soft, decreases in adhesive force, and generates residual adhesive on the adherend when the temperature is higher. Conversely, it tends to

become harder and more difficult to adhere or separate when the temperature is lower. It is evident that the urethane-based PSA changes little in hardness and has a lower temperature dependency, with the viscoelastic curve remaining relatively flat.
It is also known that the relationship between the adhesive force and peeling rate is correlated with the viscoelastic response to frequency changes[2)-3)]. For example, the viscoelastic response in the high frequency range corresponds to the behavior when the PSA is removed quickly, and the response in the low frequency range corresponds to the behavior for slow movements such as shear creep. As shown in Fig. 2, the adhesive force increases due to hardening under rapid peeling, while the shear adhesion decreases due to softening under shear-like movements in the acrylic-based PSA. However, the urethane-based PSA shows little change in adhesive force depending on the peeling rate, as it is low in frequency dependency.

Urethane-based PSAs

In a urethane-based PSA, an adhesive layer is formed by coating a solution, which is a mixture of the main agent polyol (OH), the curing agent poly isocyanate (NCO) and other additives and so forth, on the substrate such as a film and heating it to crosslink and harden. As described above, it has favorable features such as excellent oil resistance and abrasion resistance that are unique to urethane, in addition to the low dependency on time, temperature, peeling rate and so forth.
We can easily control the physical properties such as reactivity, hardness, and elastic modulus as it is comprised of two components which are the main agent and the curing agent, and it is a material with high potential with which applications in a wide range of purposes can be expected.
However, despite these excellent features, its current applications are limited due to several issues. These issues include [1] difficulty to adjust the adhesive force due to the high cohesive force of the urethane group, [2] residual adhesive on the adherent resulting from the decline in the strength of the adhesive layer when we try to improve the adhesive force by reducing the cohesive force or cross-linking density in the hard segment, and [3] difficulty in adjusting to an appropriate viscosity level due to the difficulty to increase the

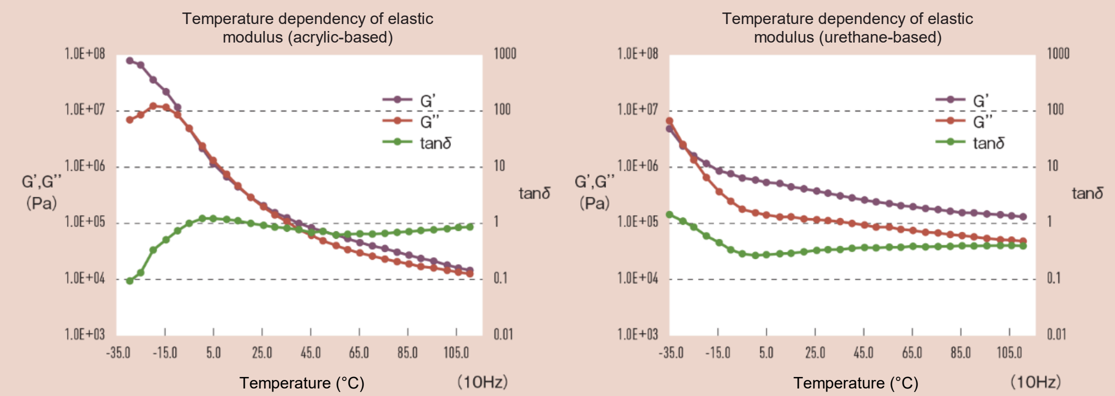

Fig. 1 **Temperature dependency of elastic modulus of acrylic-based (left) and urethane-based (right) pressure sensitive adhesives**

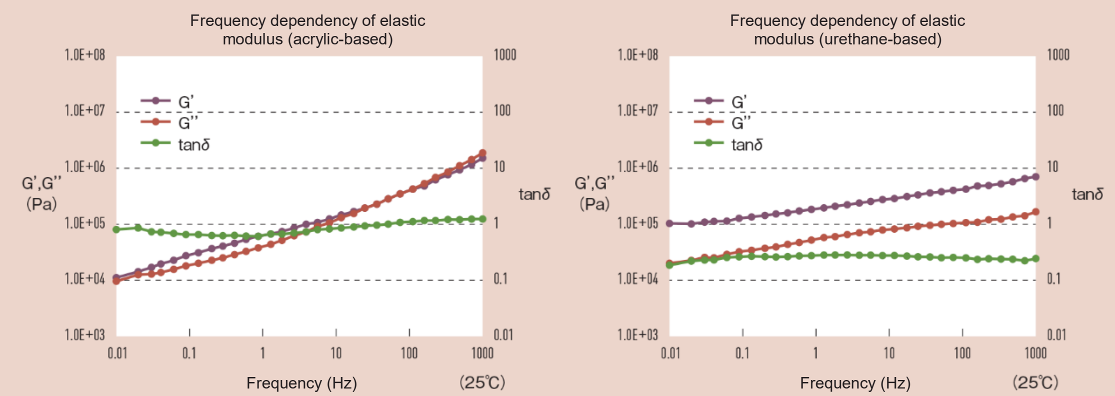

Fig. 2 **Frequency dependency of elastic modulus of acrylic-based (left) and urethane-based (right) pressure sensitive adhesives**

molecular weight.

'POLYTHIC UP' Series

Our 'POLYTHIC UP' Series (developed products) are urethane-based PSAs in which these issues have been resolved. The key to this series was the special polyol developed with our proprietary polymer design technology. We solved the issues of the conventional urethane-based PSA by significantly reducing the components present in the raw material polyol that have adverse effects on the physical properties of the PSA.

In 'POLYTHIC UP' Series, we addressed three main features using this special polyol. Fig. 3 summarizes their benefits. The details are described below.

[1] Increase in molecular weight of the prepolymer

The molecular chain entanglement effect is enhanced by the increase in the molecular weight of the prepolymer. While it is known that the entanglement of the molecular chain acts as pseudo-physical cross-linking points, it is possible to improve the elastic modulus while maintaining the viscosity since it is more fluid than chemical cross-links. This allows for the adequate membrane strength to be maintained in adhesives with medium to high adhesive force and a relatively low cross-linking density, and enables the design of urethane-based PSA with a larger adhesive force and shear adhesion and less residual adhesive on the adherent.

In addition, the molecular chain entanglement effect also exhibits a high thickening effect, and enabled us to easily adjust the viscosity, which had been difficult with the conventional urethane-based PSAs.

[2] Increase in the actual number of functional groups

Polyol undergoes side reactions in which the actual number of functional groups capable of reacting decreases during manufacture. Since the hydroxyl group at the end of polyol reacts with isocyanate and forms cross-linking, the decrease in the actual number of functional groups had caused a decrease in the cross-linking density of the PSA.

As shown in Fig. 4, it is possible to increase the cross-linking density in 'POLYTHIC UP' Series when the urethane-based PSA is cured, because the actual number of functional groups can be increased to be larger than that of the conventional polyol. This contributes to the improvement of the cohesive force and membrane strength of the PSA layer, as is the case with the molecular weight increase. In addition, based on the viewpoint of viscosity, it is possible in 'POLYTHIC UP' Series to eliminate the use of solvents in the PSA, as it is possible to secure a sufficient membrane strength with the high cross-linking density after curing, even though it was conventionally difficult to increase the molecular weight of the prepolymer in non-solvent type urethane-based PSA. Furthermore, the high cross-linking density can reduce the dependency of viscoelasticity on the temperature and frequency and address PSAs with excellent shear adhesion.

[3] Reduction in impurities and low molecular weight components

The impurities and low molecular weight components in polyol are considered a cause of increase in the adhesive force over time, contamination of the adherend, and the occurrence of residual adhesive on the adherend. 'POLYTHIC UP' Series can suppress these phenomena as these impurities and low molecular weight components have been reduced. It is therefore possible to exhibit stable PSA properties over a long period.

As described above, we solved the issues specific to urethane-based PSAs while maintaining their favorable qualities such as stable PSA properties, high oil resistance and abrasion resistance in 'POLYTHIC UP' Series. We were also able to improve the fundamental performance.

At present, we are developing two grades, which are slightly adhesive solvent type 'POLYTHIC UPW' Series and moderately adhesive non-solvent type 'POLYTHIC UPS' Series. Table 1 shows the basic physical properties of each grade. 'POLYTHIC UP' Series is capable of maintaining a stable adhering state with a wide range of adhesive forces, low in dependency on temperature, time, and peeling rate, and less likely to cause residual adhesive on the adherent. Table 2 summarizes the expected applications to utilize these PSA properties.

Future prospects

While the opportunities where urethane-based PSAs can be used have increased depending on the application, they are still lower in awareness compared to acrylic-,

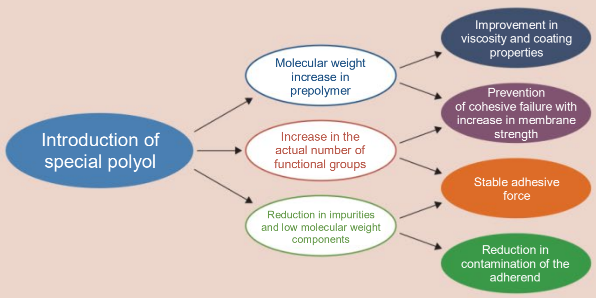

Fig. 3 Advantages addressed in urethane-based pressure sensitive adhesive with introduction of our special polyol

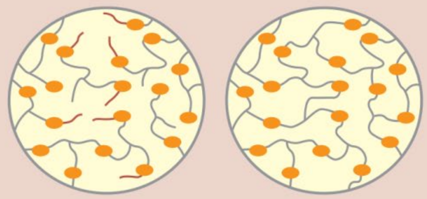

Fig. 4 Conceptual drawing of the urethane resin after cross-linking

rubber- and silicone-based adhesives. With ‘POLYTHIC UP’ Series, there are many different possible developments, such as adding functions that cannot be achieved in acrylic- or rubber-based PSAs, and replacing the expensive silicone-based PSAs. In the future, I hope that ‘POLYTHIC UP’ Series will be widely used and contribute greatly to the improvements of performance, quality, and productivity in the end products.

Reference

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Table 1 **Basic physical properties of ‘POLYTHIC UP’ Series**

		‘POLYTHIC UP’ Series (developed products)	
		Slightly adhesive type (solvent type)	Moderately adhesive type (non-solvent)
Main agent		POLYTHIC UPW-1 (prepolymer with OH end)	POLYTHIC UPS-1A (prepolymer with OH end)
Curing agent		Polyisocyanate	POLYTHIC UPS-1B (prepolymer with NCO end)
Main agent/curing agent (weight ratio)		98/2	60/40
Physical properties of the main agent	Appearance	Colorless to pale yellow liquid	Colorless to pale yellow liquid
	Viscosity (mPa•s)	Approx. 10,000	Approx. 20,000
	Pure content (%)	50 (Ethyl acetate)	100 (No solvent)
	Molecular weight Mw	Approx. 60,000	Approx. 20,000
Curing properties	Adhesive force (N/25 mm) Adhesive force on glass (adhesive membrane thickness 40 μm)	0.04	12
	Shear adhesion (mm/24 h)	0.0	0.0
	Tg (°C)	-20°C or lower	-35°C or lower
	Specific surface resistivity value (Ω)	10^8 (with antistatic agent)/ 10^{12} (no antistatic agent)	
	Moisture permeability (Method A -1) (g/m^2•day)	Approx. 3,000 (40 μm)	
	Transparency (haze)	0.3 (100 μm)	0.3 (40 μm)
	Refractive index	1.47	1.46

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Please also be sure to read the “Safety Data Sheet” (SDS) in advance.
It is the responsibility of the user to determine the suitability and safety of the product in intended application.

Table 2 **Expected application**

Adhesive force*	Application	Features of ‘POLYTHIC UP’ that can be utilized
Slightly to weakly adhesive	Protective film to prevent damage and contamination during manufacture and shipment of electronic materials, optical films, etc.	Stability of pressure-sensitive adhesive properties, removability, and low contamination Urethane film strength, antistatic properties
	Binding and masking of components for automobiles and buildings	Stability of pressure-sensitive adhesive properties, durability and weather resistance
Moderately to highly adhesive	Binding of touch panel, display parts, etc.	Stability of pressure-sensitive adhesive properties, low contamination Low temperature dependency
	Retention and transport of electrical and electronic components and optical components for processing in the next process	Stability of pressure-sensitive adhesive properties, low contamination, and removability Low peeling rate dependency, antistatic properties
	Use as adhesive tapes for fixing medical tubes and catheters, medical film dressing material for bedsore treatment, etc., surgical tape, adhesive plaster, wearable applications, etc.	Improves the comfort as it contains little residual monomer or solvent compared to acrylic-based ones, is low in odor or skin irritation, and has high moisture permeability[4]

* Although there is no specific rule on the expression of adhesive force, the adhesive force to glass is defined based on the following classifications in this article. Slightly adhesive: 0.1 N/25 mm or lower, weakly adhesive: 0.1 to 5 N/25 mm, moderately adhesive: 5 to 10 N/25 mm, highly adhesive: 10 N/25 mm or higher. For reference, common sticky notes are weakly adhesive, cellophane tapes are moderately adhesive, and gummed tapes are highly adhesive.