One-component polyurethane adhesive: Rheological behavior & mechanical properties

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Introduction

One-component polyurethane adhesive(1-C PUR), known as its molecular-adjustable, fast-curing and strong-bonding, is getting widely used in construction and automotive industry[1]. One of the key issues would be the effect of thixotropic agents on rheological behaviors and mechanical properties, which is instructive and meaningful to optimize process and formula. However, few effort was made to clearly understand how fumed silica affects the 1-C PUR rheology and the complicated interaction varies between particles and liquids. Hence, it is of academic and practical importance to give a reasonable interpretation in shear thinning-thickening mechanism of 1-C PUR.

In this work, the effect of (1)surface treatment of fumed silica; (2)volume of particles; (3)liquid viscosity; (4)curing catalyst on the shear/strain-thinning and thickening behavior are explored. The aspects above exhibit significant influence on the shear response of 1-C PUR. Such a vary-formulary attempt is of great significance for manufacturing guidelines in coating and adhesive industry.

Experimental

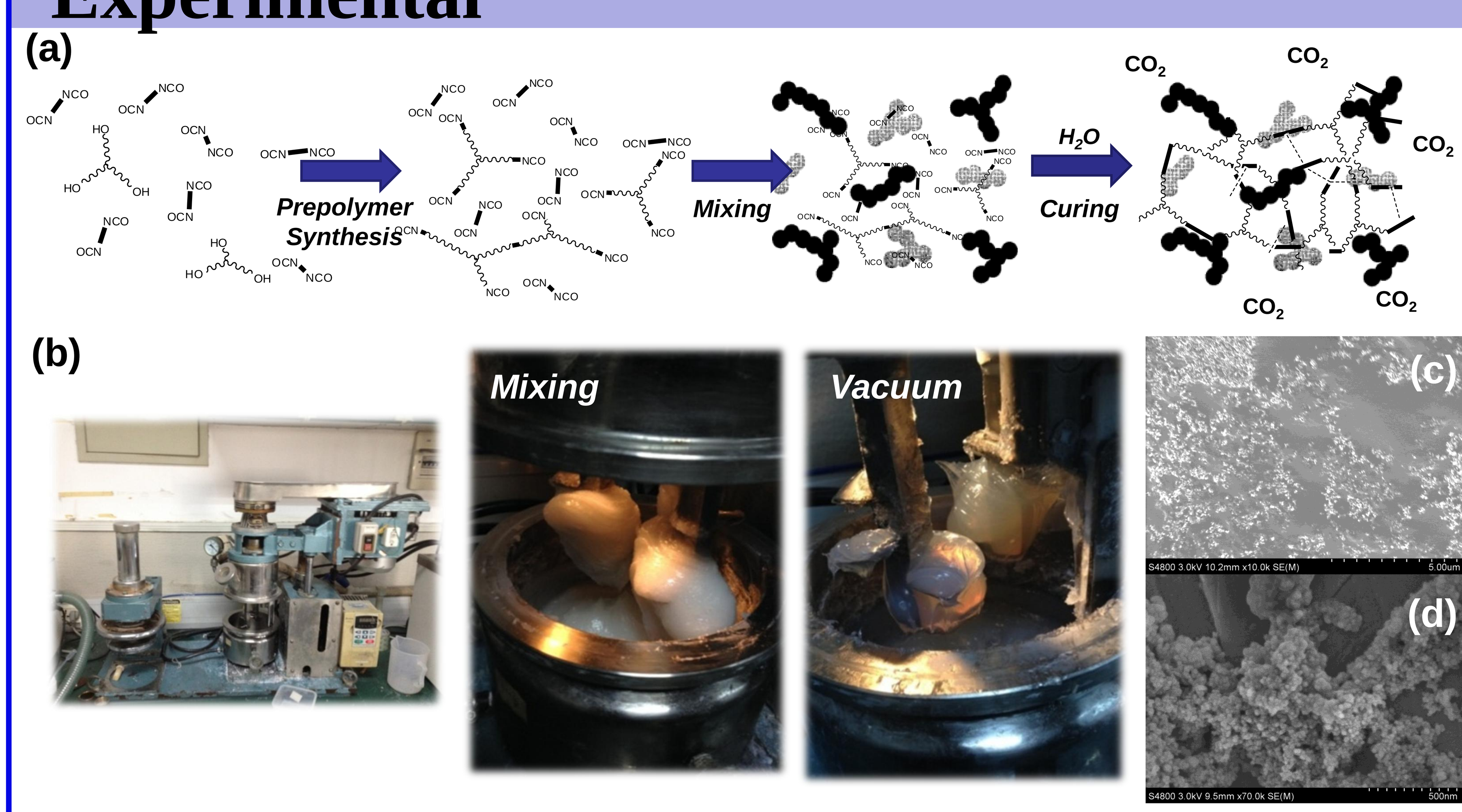

Fig. 1. Synthesis and process of 1-C PUR. (a) Scheme of prepolymer synthesis, mixed with fumed silica and curing; (b) Planetary mixer for synthesis and mixing; (c) Micrograph (SEM) of 1-C PUR; (d) Fumed silica powder centrifuged from 1-C PUR & toluene solution.

Results and Discussion

I. The effect of surface treatment

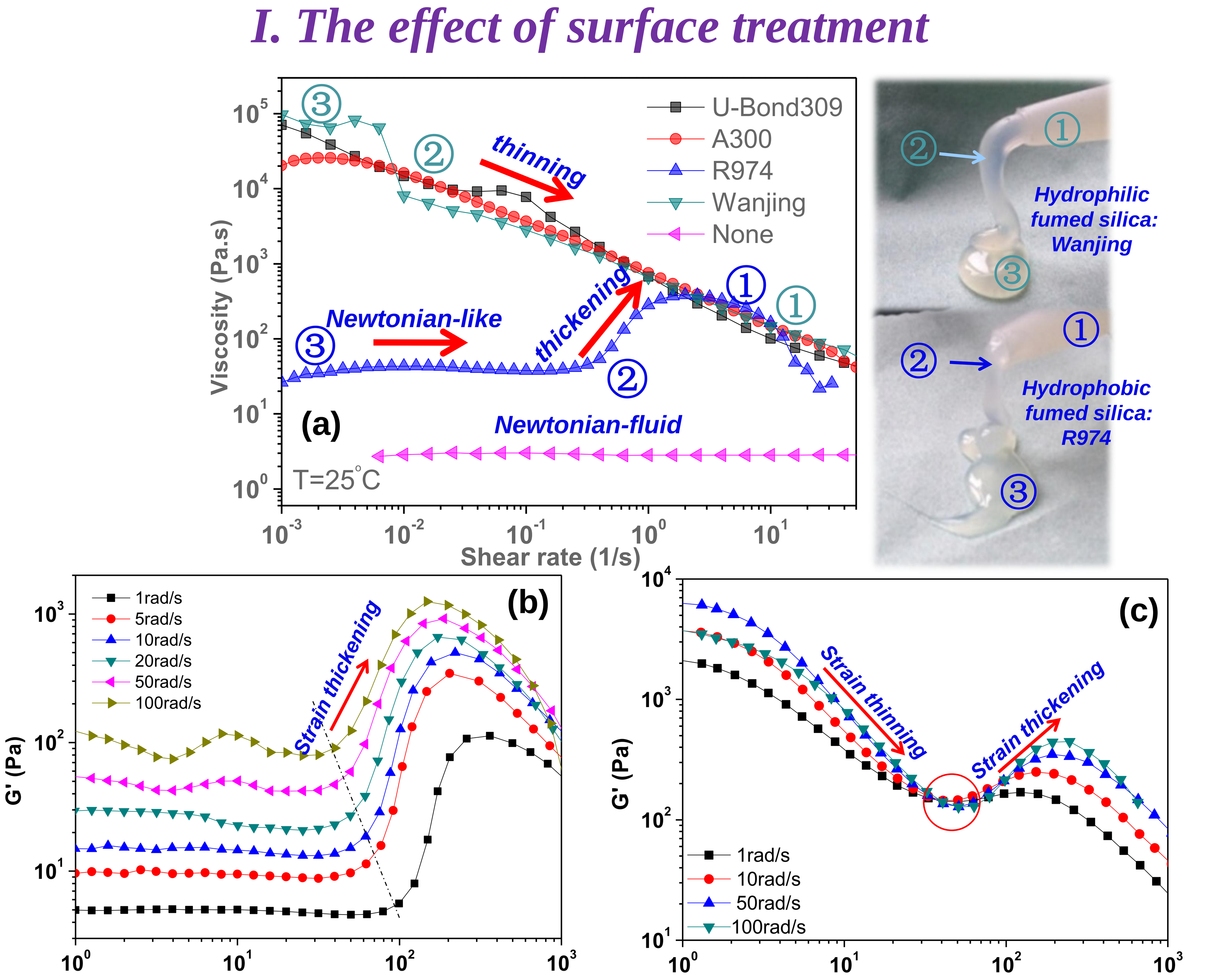

Fig. 2. (a)Shear rate dependence of viscosity for different fumed silica suspensions; G' as a function of strain amplitude conducted at different frequencies for fumed silica- prepolymer A suspension. (b)R974(hydrophobic) 10 parts by mass; (c) A300(hydrophilic) 10 parts by mass

II. The effect of addition amount

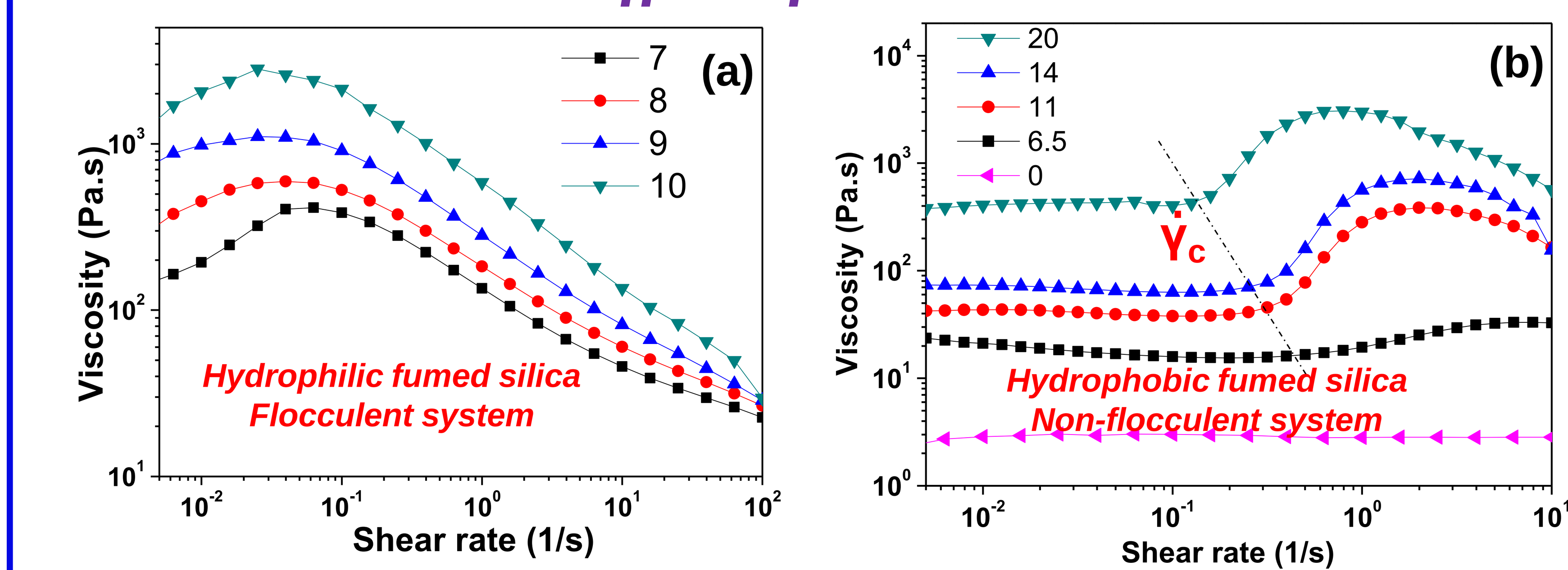

Fig. 3. Shear rate dependence of viscosity for different fumed silica suspensions; (a)Wanjing; (b) R974 with different parts by mass.

III. The effect of liquid viscosity/catalyst

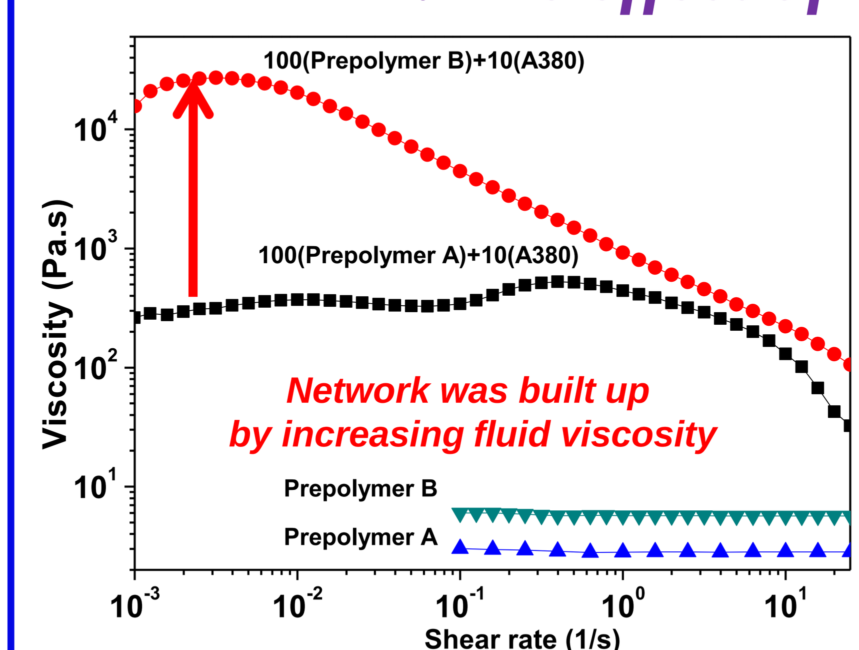

Fig. 4. Shear rate dependence of viscosity for different prepolymer (A: LMDI+N330, NCO%=10%; and B:LMDI+N330+DL400, NCO=10%) with different viscosity.

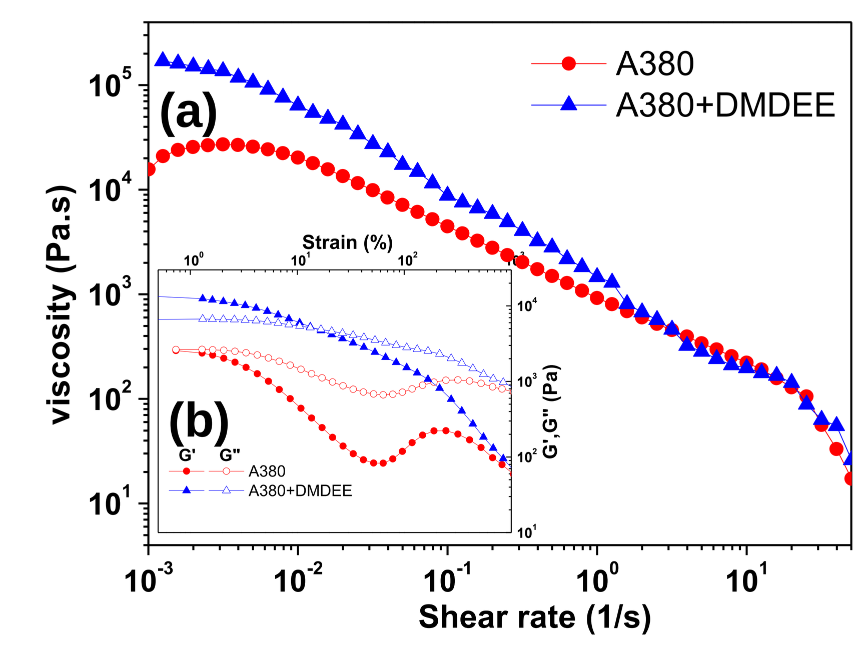

Fig. 5. Rheology of A380 suspension with/without DMDEE. (a) Shear rate dependence of viscosity; (b) Elastic G' and viscous G" as a function of strain amplitude, frequency=1rad/s.

IV. The storage stability

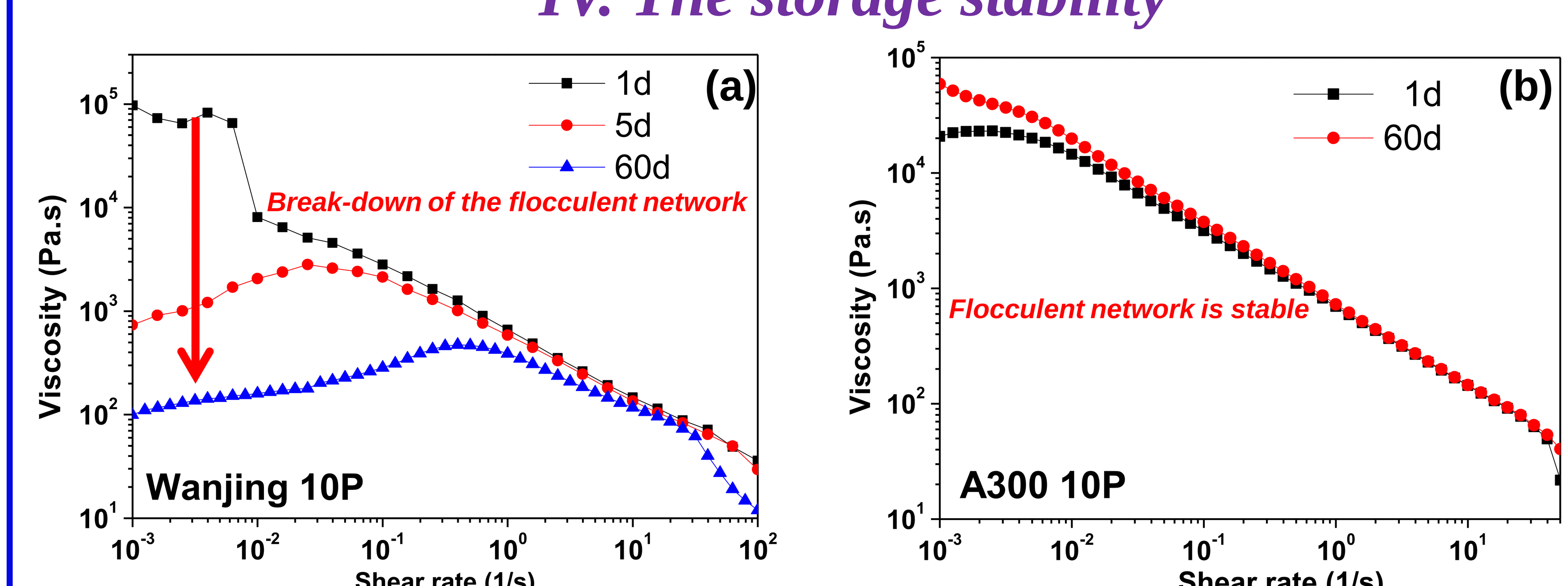

Fig. 6. Shear rate dependence of viscosity for different storage time. (a) Wanjing 10 parts by mass; (b) A300 10 parts by mass.

Conclusions

- *Fumed silica with different surface (hydrophilic or hydrophobic) treatment exhibit dramatic different rheological behavior, either flocculent or not when dispersed into PU prepolymer.*
- *Non-flocculent suspensions show both shear and strain thickening behavior, while flocculent suspensions show continuous shear thinning during steady flow and complicated rheology behavior through oscillating shear. Fig.6 gives appropriate explanation of shear thinning-thickening behavior. The mechanism will be further discussed.*
- *The prepolymer viscosity shows significant effect on the flocculate network. High viscosity liquid can even help to build the flocculent structure.*

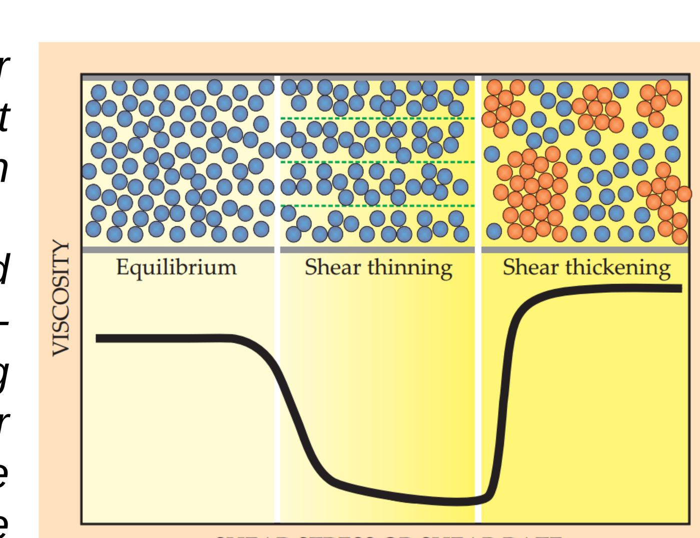

Fig. 7. Explanation of shear thinning-thickening behavior in concentrated colloidal suspensions[2]

- *Catalysts: DMDEE(tertiary amine) thickened the system and made the flocculation stronger while DBTDL(organotin) damaged the network between silica particles.*
- *The storage stability of flocculent sample must be taken into account since slow reaction between silicol group and –NCO could damage the network built by the hydrogen-bond between silica particles.*

References

[1] Malucelli G, Priola A, Ferrero F, et al. Polyurethane resin-based adhesives: curing reaction and properties of cured systems[J]. International Journal of Adhesion and Adhesives, 2005, 25(1): 87-91.

[2] Wagner N J, Brady J F. Shear thickening in colloidal dispersions[J]. Physics Today, 2009, 62(10): 27-32.