

Studies on liquefaction of agricultural wastes and their application for preparing polyurethane foam

(農業廃棄物の液化とそれを用いたポリウレタンフォームの調製に関する研究)

Four kinds of representative agricultural straw, rice straw (RS), oilseed rape straw (OS), wheat straw (WS) and corn stover (CS), as common visible biomass, are large amounts and show low utilization value. Hence using of these wastes has become to be an environmental and economic hotspot recently. Besides of fermentation, gasification and pyrolysis of biomass, biomass liquefaction technology has attracted great attention as its simple operation, high production level and high energy conversion. The obtained liquid product, bio-polyol, has been researched to prepare phenolic resin, polyurethane, epoxy resin and carbon fiber till now. This study focuses on agricultural wastes liquefaction technology and application of the liquid products to prepare polyurethane foam.

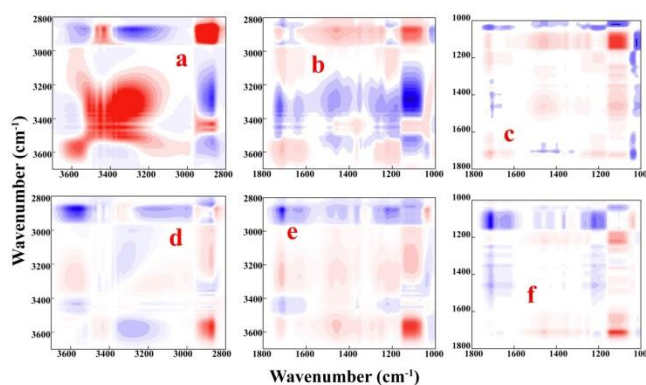
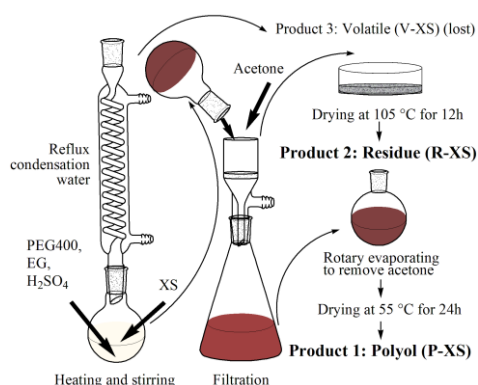


Fig. 1 Liquefaction process and product separation

Fig.2 2D-COS contour maps of P-OS-c_{H2SO4}

In chapter 2, RS, OS, WS and CS are chosen to be liquefied by polyethylene glycol 400 (PEG400) and ethylene glycol (EG) mixture solvents with sulfuric acid as catalyst under atmospheric pressure. The liquefaction process (Fig.1) is optimized by changing reaction parameters (ratio of liquid and solid/ $m_L:m_S$, straw particle size, ratio between PEG and EG/ $m_{PEG}:m_{EG}$, catalyst dosage/ $c_{H_2SO_4}$, reaction temperature/ T and reaction time/ t) to achieve a high liquefaction conversion and obtain excellent products. For confirming the optimal liquefaction process, biomass conversion ratio, products distribution, recycled acetone ratio and liquid product properties are investigated respectively. Results show that liquefaction conversion ratio is influenced by temperature and $c_{H_2SO_4}$ significantly, while $m_L:m_S$, XS particle size (XS: RS, OS, WS or CS), $m_{PEG}:m_{EG}$, and time show less influence on conversion ratio. An optimal liquefaction process is confirmed as 7:1 of $m_L:m_S$; bigger than 40 mesh of RS, WS or CS and 40~100 mesh of OS; 3/1 of $m_{PEG}:m_{EG}$; 3% of $c_{H_2SO_4}$; 150 °C

of T and 40 min of t, with conversion ratios of RS, OS, WS and CS are 79.1%, 93.7%, 88.3% and 87.4% respectively.

In chapter 3, XS liquefaction products are investigated by FT-IR and two dimensional correlate spectroscopy (2D-COS) IR (Fig.2) to investigate chemical bonds change regularities during liquefaction process. Potential reactive groups in XS are converted into bio-polyol while ash is concentrated in residue. Some coking reactions occur at too low $m_L:m_S$. Departing of O-H, C-H groups and disruptions of aromatic C=C groups from lignin in XS are promoted visibly, while departing of C=O groups from hemicellulose is promoted mildly when enhanced $m_L:m_S$. XS particle size displays mild influence on XS liquefaction process and products components. 3/1 of $m_{PEG}:m_{EG}$ appears the best liquefaction efficiency to transform XS. Dissolving of O-H or C-H containing structures is mainly promoted among 1~3% of catalyst. Degradations of structures contained C=O and C=C groups are accelerated obviously at 120 °C, while transformations of O-H, C-H, C=O and C=C are promoted enormously at 150 °C. Degradations of unsaturated structure are mainly occurred at first 10 min or 20 min in RS or OS liquefaction. Transformations of O-H bonds are among 0~40 min and mainly occurring among 20~30 min of liquefying time. According to 2D-COS IR, O-H and C-H bonds in P-OS appear more active than in P-RS with changing of $c_{H_2SO_4}$. Aromatic ring structures appear more susceptible towards catalyst in R-OS than that in R-RS. C=CH, C-H, C-C and O-H bonds trend to convert into P-XS at higher temperature. Structures contained -COOH, substituted -Ar-H, SO_4^{2-} and Si_xO_y trend to remain in R-RS, while SO_4^{2-} and CO_3^{2-} appear to leave in R-OS after liquefaction at higher temperature. Structures contained O-H, C=O, C=CH, C-H and C-C trend to be transformed into P-XS, while C-O-C and Si_xO_y , or -COOH and CO_3^{2-} containing structures lean to keep in R-XS with prolonging of liquefying time.

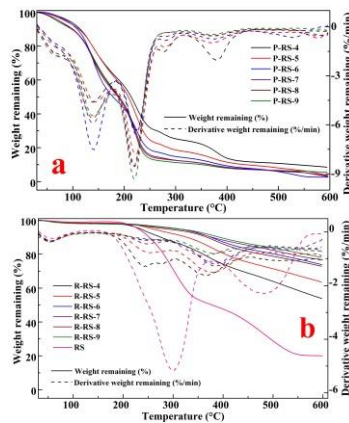


Fig.3 TG-DTG of P-RS- $m_L:m_S$ and R-RS- $m_L:m_S$

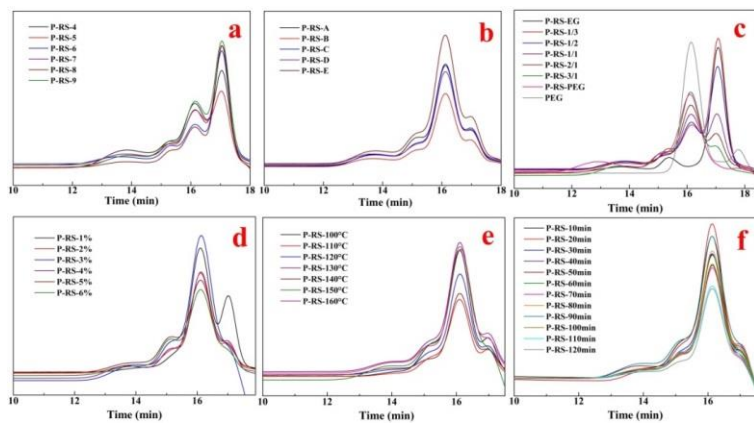


Fig.4 GPC curves of P-RS-p

In chapter 4, XS liquefaction products are investigated by Thermogravimetric analysis (TGA) and Gel permeation chromatography (GPC) (Fig.3 and Fig.4) to investigate their thermal stability and molecular weight change regularities during liquefaction process. Liquefied agricultural wastes polyols degrades or evaporates among five regions 30~100 °C, 100~170 °C, 170~315 °C, 315~430 °C and 430~600 °C. Four parts of components containing in the polyol, they show Mw around 25900~9000 g/mol (XS derivatives, lignocellulose

fractions), 2600~1310 g/mol (lignocellulose fraction degradation products), 717~412 g/mol (PEG and its derivatives) and 105~81 g/mol (EG and its derivatives) respectively.

In chapter 5, oilseed rape straw liquefied polyol is used to react with isocyanate for preparing PU foam. Foaming process (Fig. 5) is optimized by investigating effects of NCO/OH ratio, catalyst dosage, surfactant and blowing agent. The prepared foams are evaluated by foaming stage, density, compression test, Scanning electron microscope (SEM), Dynamic mechanical analysis (DMA), water absorption ability and TGA test. 1.7 of NCO/OH ratio, 4% of surfactant, 1% of blowing agent and 3% of catalyst are confirmed as optimal formulas for preparing OS polyol based PU foam. Surfactant controls foam cell type and shape, blowing agent controls cell size and wall thickness, catalyst controls cell size, while polyol dosage influences foam structure gravely. The optimal foam appears applicable density, comparable compression strength, high elastic modulus, uniform cellular structure, better thermal stability and excellent water absorption ability.

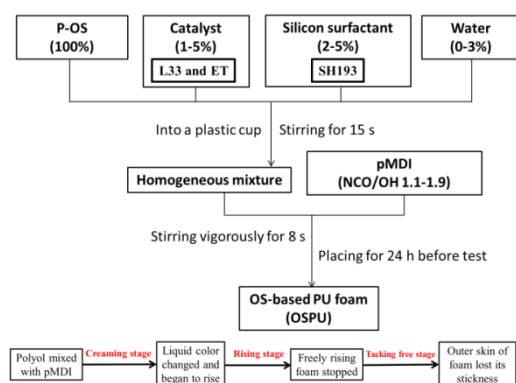


Fig.5 OSPU foam preparation process

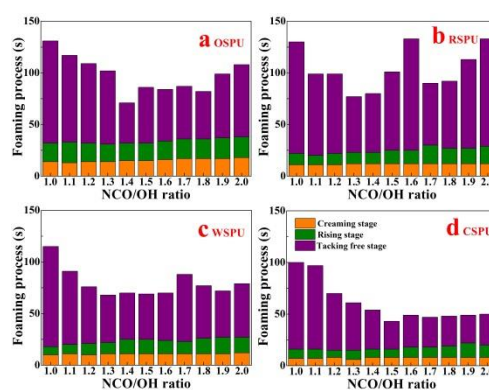


Fig.6 XSPU foaming stages with different NCO/OH ratio

In chapter 6, four kinds of agricultural wastes based polyols, are used to replace petroleum based polyol and prepare PU foam successfully. The effect of NCO/OH on PU foaming process (Fig. 6) and foams properties are investigated. CS based polyol appears the highest reactivity to react with pMDI, while reactivity of OS based polyol is the lowest. Foams made with NCO/OH ratio among 1.4~1.7 appear excellent morphological, physical, mechanical, water absorption and chemical properties.

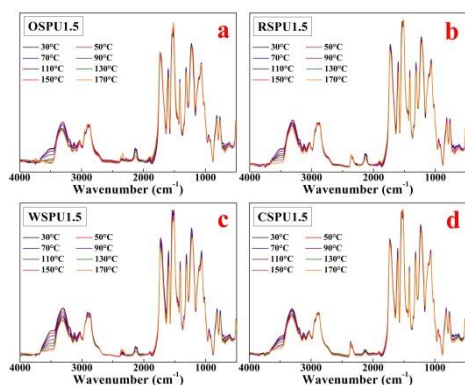


Fig.7 FT-IR of XSPU1.5 (heating among 30~170° C)

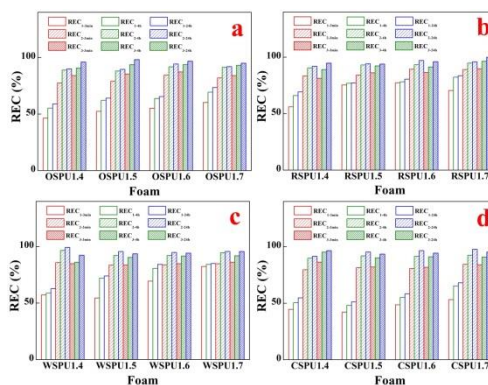


Fig.8 XSPU recovery ability after compression

In chapter 7, thermal stability, stability in water, stability in soil and compression recovery ability of XSPU are explored by TGA, FT-IR, water immersion test, soil burying

test and compression test (Fig.7 and Fig.8) respectively. The prepared four kinds of bio-based foams appear excellent thermal stability. Hydrogen bond has a great influence on the thermal stability of foam. Foams appear almost no weight change and more hydrogen bonds are established when immersed them in water. Degradability of these foams in soil is significantly higher than petroleum polyol based PU foam, as its soft segments are easier to be mineralized. Compression recovery ability of XSPU after 1~3 times of compression test appears about 48.1~99.9%, which show potential to be used as elastomer.

In chapter 8, the smallest XS particles (smaller than 100 mesh) were used to reinforce XSPU foams. Different XS loading amounts among 0~15% are investigated to confirm suitable filler concentrations for modifying XSPU foams (Table 1). RS particles show the greatest promoting ability, OS particles appear a complex influence, while WS and CS particles display mild effect on bio-based PU foaming process. With 1% of OS, 6% of RS, 3% of WS or 1% of CS particles incorporating in matrix materials, the reinforced PU foams could reach a better mechanical property, more uniform cellular structure, thermal stability and chemical stability without huge changing of water absorption ability.

Table 1 Selected properties of XSPU1.5 and reinforced XSPU1.5 foams

Foam	Density (kg/m ³)	Compressive strength (kPa)	Elastic modulus (MPa)	Average cell size (μ m)	Storage modulus (MPa)	Tg (° C)
OSPU1.5	19.7	47.0	1.22	314	1.48	154
OSPU1.5-1%OS	20.1	39.2	0.66	272	2.61	160
OSPU1.5-3%OS	20.5	29.6	0.49	259	2.33	163
OSPU1.5-6%OS	18.9	30.1	0.59	215	1.98	165
OSPU1.5-10%OS	19.9	33.5	0.68	219	3.11	174
OSPU1.5-15%OS	21.3	20.8	0.39	227	1.46	177
RSPU1.5	27.1	31.9	0.43	269	0.67	145
RSPU1.5-1%RS	23.3	38.9	0.75	262	0.96	175
RSPU1.5-3%RS	20.8	45.4	0.76	262	0.87	177
RSPU1.5-6%RS	21.1	52.3	0.83	271	0.78	199
RSPU1.5-10%RS	23.5	25.3	0.38	200	0.80	188
RSPU1.5-15%RS	21.2	36.8	0.64	212	1.79	176
WSPU1.5	23.1	26.7	0.56	265	0.66	154
WSPU1.5-1%WS	19.9	27.7	0.55	230	0.71	165
WSPU1.5-3%WS	20.6	30.2	0.54	250	1.00	157
WSPU1.5-6%WS	20.0	22.9	0.37	222	0.86	163
WSPU1.5-10%WS	22.1	27.0	0.45	197	0.97	160
WSPU1.5-15%WS	20.9	35.9	0.61	257	1.40	179
CSPU1.5	18.9	46.1	0.77	317	0.88	143
CSPU1.5-1%CS	19.8	25.7	0.44	220	0.92	154
CSPU1.5-3%CS	17.1	27.7	0.54	295	0.97	146
CSPU1.5-6%CS	18.0	22.3	0.35	274	1.14	151
CSPU1.5-10%CS	17.4	22.6	0.38	250	1.36	165
CSPU1.5-15%CS	16.9	22.7	0.38	244	1.74	167

Generally, an optimal liquefaction process design is confirmed to convert four agricultural wastes with high conversion ratio. The obtained polyols appear suitable hydroxyl number, acid number, viscosity and molecular weight to replace petroleum based polyol for synthesizing polymers. Four kinds of foams are prepared successfully, and these foams appear applicable density, comparable compression strength, high elastic modulus, uniform cellular structure, fine thermal stability and excellent water absorption ability to apply in industry and daily life. Reinforced XSPU1.5 foams with more uniform cellular structure, better physical and mechanical ability or finer thermal stability could be obtained when used moderate XS particles as reinforcement fillers.