

Recycled Polyurethane NanoPowders as Active Extenders of UF and PF Wood Panel Adhesives

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Abstract

The addition to urea-formaldehyde (UF) resins and to phenol-formaldehyde (PF) resins of micronized polyurethane nanopowders obtained from waste flexible polyurethanes improve markedly the performance of the panels prepared with these resins, namely plywood and particleboard. Infrared spectrophotometry (FT-IR) indicates that a reaction does appear to occur to some limited extent between micronized PUR waste powder and PF resin when the mix is cured under alkaline conditions. There appear to be no reaction at all instead between acid-setting UF resins and PUR powder. In both cases a active filler or extender effect appears to occur, otherwise the improvement in dry strength of UF-bonded joints cannot be explained. Even when reaction does evidently not occur the addition of PUR powder improves markedly the water resistance of UF and PF resins. This active extender/filler effect is not due to any isocyanate group being re-generated on heating as both FT-IR and NMR confirm the absence of these groups.

1. Introduction

The flexible polyurethane foam market is a 3 million tons/year global industry serving furniture, bedding and automotive applications, as well as many other smaller users. The process of manufacture of polyurethane foam generates a considerable amount of non-saleable product (Berthevas et al 2005). Manufacturing trimmings and off-cuts, called trim foam, typically represent between 15% and 20% of total foam production. Industry statistics suggest that availability of waste trim foam, thus trim foam not used for useful purposes, currently at almost 300 000 tons/year in the USA is likely to increase to more than 400 000 tons/year in the near future (Berthevas et al 2005).

Various chemical alternatives to break down trim foam to polyols for re-use in polyurethane manufacture have been proposed, but they have all met with rather limited success (Bauer et al 1999, Berthevas et al 2001, Shutov 1999, Weigand et al 1993, You et al 1997). One different method proposed more recently consists in pulverizing the PU foam scraps at ambient temperature into a micronized powder, followed by the separation of the fine from the coarser particles (Neuray et al 2000, Stone et al 2000, Wagner et al 1994). One of these processes is the Mobius Technologies process using a 2-roll-mill to pulverize the PU foam scraps (Berthevas et al

2004, Martel et al. 2003, Stone et al 2000, Villwock et al 2001). It has now been, in commercial operation in North America and Europe for a few years already (Berthevas et al 2005). Manners to use this waste resource are always sought.

Recently, pulverized micronized Mobius PU powders were used in conjunction with polymeric isocyanate (PMDI) to replace PMDI used as binder in particleboard preparation (Berthevas et al 2005). This work indicated that a 10% to 20% substitution of PMDI by PU powder gave good results satisfying the relevant board standards for IB strength (European Norm EN 312-5 and 7). The results indicated, among other possible effects, that heterogeneous reaction between the amino functions of the waste PUR powder and the isocyanate groups of PMDI to include the PUR powder in the crosslinked isocyanate network is possible (Berthevas et al 2005).

The reaction between PMDI and formaldehyde-based resins in water is now well known [Pizzi and Walton 1992, Huntsmann Polyurethanes 2006, Despres et al 2006, Wieland et al 2006, Simon 2002]. However, in these mixes, a second type of cross-linking reaction has been reported, generally masked by the main reaction between the isocyanate group and the methylol group of the two resins. This is the reaction of the methylol group of an aldehyde-based resin, such as UFs and PFs, on the *ortho* or *para* available sites of the aromatic ring of PMDI (polymeric 4,4'-diphenylmethane diisocyanate). These sites are activated by the presence of either the isocyanate group ($-N=C=O$) or of the $-NH-$ group of the urethane bridge. It is to check this hypothesis and to study if UF and PF adhesives could be partly substituted by micronized PUR powder, with or without participation to cross linking that the research reported in this paper was undertaken.

2. Experimental

A commercial UF resin for plywood of F/U molar ratio 1.2 and a PF resins of F/P molar ratio of 1.7 manufactured according to a procedure and proportions already reported (Pizzi and Stephanou 1993) were used. A micronized PUR powder supplied by Dow Chemicals and Mobius Technologies were used.

Duplicate, one layer laboratory particleboard of dimension 350x350x14 mm were prepared. The total resin solids by weight onto the wood particles was of 9 % for the PF resin, at a pressing time of 7.5 minutes, 195°C with maximum pressure of 25 kg/cm². Aimed board density was 690 kg/m³. The boards were tested according to European Norm EN 312-5 and -7 for internal bond (IB) strength dry and after 2 hours boiling.

Duplicate 3-ply beech veneer laboratory plywood of dimensions 450x450x6 mm were prepared adding to the UF resin different weight percentage proportions on resin solids content of wheat flour and/or micronized PUR powder as indicated in Tables 1 and 2. 2% ammonium sulphate

hardener on resin solids content used as a 30% water solution was used as hardener. Glue mix load double glue lines was of 320 g/m^2 . Pressing conditions were 5 minutes at 120°C and 11 kg/cm^2 . After cutting the samples were tested in tension dry, after 24 hours cold water soak and after a number of minutes in boiling water to check after how many minutes they would delaminate.

Duplicate 3-ply beech veneer laboratory plywood of dimensions $450 \times 450 \times 6 \text{ mm}$ were prepared adding to the PF resin 20% by weight on resin solids content of 200 mesh wood flour or micronized PUR powder. Glue mix load double glue lines was of 350 g/m^2 . 5% triacetin ester accelerator was added to the slow PF resin used. Pressing conditions were 10 minutes at 150°C and 15 kg/cm^2 . After cutting the samples were tested in tension dry, after 24 hours cold water soak and after 6 hours in boiling water, tested wet.

The solid state FT-IR analysis of the hardened UF, PF and PUR controls and of the hardened UF/PUR (70/30 and 60/40 by weight) and PF/PUR (70/30 and 60/40 by weight) resin systems used, were obtained by preparing KBr pills, on a Shimadzu FT-IR 8200 infrared spectrophotometer.

The solid state ^{13}C NMR spectra of the hardened UF, PF and PUR controls and of the hardened UF/PUR (70/30 and 60/40 by weight) and PF/PUR (70/30 and 60/40 by weight) resin systems used, were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at sample spin of 4.0 kHz. The impulse duration at 90° was $4.2 \mu\text{s}$, contact time was 1 ms, number of transients was about 1000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control.

3. Results and Discussion

The results of plywood in which PUR micronized powder was either added additionally or substituted for wheat flour (UF bonded panels) and to wood flour (PF bonded panels) fillers are shown in Tables 1 and 2. In Table 1 the introduction of the very fine PUR powder in the place of wheat flour had the effect of somewhat upgrading the water resistance of the UF-bonded plywood. Polyurethane waste powders are water repellent. It is then expected that by substituting them to wheat flour a better resistance to water of the UF bonded joint would result. Both dry tensile strength and tensile strength after 24 hours cold water soak in the case of PUR powder show an improvement over the controls based only on wheat flour addition. Further improvement of dry and cold water soak tensile strength is obtained by adding in certain proportions both PUR and wheat flour to the UF plywood resin. Thus a 40% PUR + 10% wheat flour addition on UF resin solids content yields a marked improvement in dry and cold water soak tensile strength, as well as the best resistance to boiling water (Table 1).

An equivalent test on PF-bonded plywood in which wood flour was substituted by PUR micronized powder also yielded improved results, and this time the differences are statistically significant; both when the panels were tested dry and wet after 24 hours of cold water soaking and 6 hours immersion in boiling water (Table 2). The increase in wet properties of the joint could be expected, given the water repellency of the polyurethane powders. What is remarkable instead is the marked improvement in dry strength of the panels. This might infer that reaction between the powder and the resin might occur, although other valid explanations could also exist.

The results of a comparative study in which particleboard were prepared by partially and progressively substituting the PF resin itself with the PUR powder, on the same basis of the substitution experiment of PMDI with PUR (Berthevas et al 2005), are presented in Table 3. IB strength after 2 hours of boiling is 55% higher for a 22% substitution of PF resin by the PUR powder, while maintaining dry IB strength the same as the control. A substitution level of 11% yields 28% improvement in 6 hours boil IB strength and 13% improvement in dry IB strength. In both cases a noticeable decrease of the PF resin by substituting it with the cheaper waste PUR powder is possible. Higher substitution, namely up to 33% of the PF by the PUR powder yields much worse results than the control. This is an indication that the PUR powder markedly is a much less effective adhesive than the PF resin, allowing only a limited, but still consequent, level of substitution. Such behaviour is possibly that of an active, reactive extender, quite possibly not that of an adhesive and definitely not that of a filler.

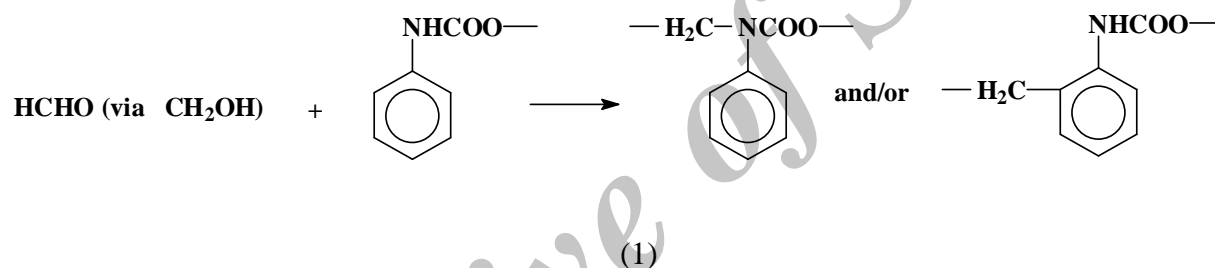
The results in Table 1, 2 and 3, namely the unexpected and remarkable improvements in dry strength of the panels coupled with their improvement in water resistance raise the question of how the PUR powder does act. Does a heterogeneous phase reaction between the methylol groups of the UF and PF adhesive with the aromatic ring and amido groups of the hardened PUR powder really occur? And if so, to what extent? Or is the PUR only a very good filler? Does the pH of hardening, acid for UF resins, alkaline for PF resins influence the results or a hypothetical reaction?

To answer these questions solid phase infrared (FT-IR) and ^{13}C NMR analysis on the hardened UF/PUR and PF/PUR mixes were done. The UF (or PF): PUR weight ratio was of 1: 0.3 and 1:0.4.

In Figs. 1, 2 and 3 the FT-IR spectra of the PF resin, the PUR powder and of the co-hardened PF+ 40% PUR mix are shown. In Fig. 3 the differences which occur in relation to the original material are small but interesting. One of the $>\text{C}=\text{O}$ (the double peak at $1700\text{-}1730\text{ cm}^{-1}$) of the polyurethane is much smaller, almost disappearing. The other $>\text{C}=\text{O}$ peak from the polyurethane, at 1650 cm^{-1} becomes markedly smaller. This peak overlaps also the 1650 cm^{-1} peak of the $\text{C}=\text{O}$ of the free formaldehyde of the PF resin alone. Its marked decrease indicates a marked decrease of the free formaldehyde present in the system. The 1550 cm^{-1} peak belonging to the methylene groups of the PUR constituent polyol becomes also markedly smaller. The decrease of both these two peaks is such that the small peak of the PUR $>\text{C}=\text{O}$ at 1600 cm^{-1} in Fig. 2, which remains unaltered, becomes in Fig. 3 the dominant one of the PUR carbonyls in the PF/PUF mix. This means that there is a decrease, to some extent of at least two types of carbonyl groups of the polyurethane. Other than the $\text{C}=\text{O}$ of unreacted isocyanate groups at 2250 cm^{-1} region (there are

none in Figs. 2 and 3), there are three possible C=O groups in polyurethanes, those belonging to the urethane bridge, those to carbamic acid intermediates immobilized in the network, and those belonging to biuret, allophenates and substituted ureas. One of these does not vary, logically that belonging to biuret, allophenate and substituted ureas. This means that the urethane bridge content and the traces of carbamic acid intermediate decrease. The latter is logical due to the presence and reaction with water coming from the PF resin. The former instead is indicative of a reaction occurring. The reactions possible to fit this are first of all a decrease of the urethane linkage, the only alternative being a reaction of hydrolysis of the urethane bridge in presence of the considerable amount of water of the PF resin and its reaction with this water to form ammine and ultimately polyureas and biurets, as would be expected in isocyanate and urethane chemistry. Reactions of transesterification involving the urethane bridge do not appear possible as the decrease of urethane groups observed by FT-IR does not support this hypothesis.

However the 1650 cm^{-1} peak also represents unreacted formaldehyde $-\text{CHO}$ carbonyl. Its decrease indicates that this formaldehyde can react with both the aromatic ring of the PF resin or with that of the PMDI (which is more activated by the isocyanate or amidogroup of the urethane) to give methylene cross-links of the type:



A confirmation of this reaction comes from the decrease of the dimethylene ether peak at 1280 cm^{-1} from PF alone (Fig. 1) to PF/PUR (Fig. 3) indicating rearrangement of these bridges to methylene bridges. This results in liberation of further free formaldehyde, that will be consumed reacting as in reaction (1). No other reaction of note appears possible from the FT-IR spectra. It is not possible to evaluate the extent of reaction (1) above from the IR spectra presented.

No differences were noticeable between the two FT-IR spectra of the UF resin and of the UF/PUR resin mix (for this reason they are not reported here). This indicates that in the case of the UF resin the micronized PUR powder has functioned just as a filler/extender. No reaction between the two appear to have occurred. The difference with the PF case can be ascribed to the different pHs of operation of the UF and PF resins. UF resins are acid-setting (pH 4) while PF resins for wood are alkaline-setting (pH 11-13). ^{13}C NMR were done of both systems. They indicated no reaction at all in the case of the UF/PUR system (hence spectra are not reported here). In Fig. 4 and 5 are shown the comparative solid state CP-MAS NMR spectra of PUR powder, PF resin and the 70/30 PF/PUR. There is only one interesting difference: the $-\text{CH}_2\text{OH}$ band at 65-66 ppm decreases passing from the PF resin to the PF/PUR mix. This is a confirmation that reaction (1) does exist, under alkaline curing conditions. It is impossible from these data to define its extent.

4. Conclusion

In conclusion, some reaction does appear to occur between micronized PUR waste powder and PF resin when the mix is cured under alkaline conditions. There appear to be no reaction at all between acid-setting UF resins and PUR powder. In both cases a active filler or extender effect appears to occur, otherwise the improvement in dry strength of UF-bonded joints cannot be explained. Even when reaction does evidently not occur the addition of PUR powder improves the water resistance of UF and PF resins. This is particularly useful for the UF resin case where addition of a waste, inexpensive material avoid the use of foodstuff, wheat flour, for the same use and with much improved results. This active extender/filler effect is not due to any isocyanate group being re-generated on heating as both FT-IR and NMR confirm the absence of these groups. The only opinion that could be advanced is that some surface flow, a surfaces stickiness/melting of the PUR powder might occur with the surface material behaving as a thermoplastic and improving adhesion. These PUR powder have been found to partially melt and bond wood by friction welding although at much higher temperatures than what used in this article (Pichelin 2006). It is impossible to verify this with the present data but the PUR powder itself does not melt in its bulk at the panel temperatures used.

References

- Bauer G, Kugler M, Chakrabarti RS (1999) Recycling of PUR flexible foams: solvolysis with carboxylic acids fills the gap. *Kunststoffe* 89(2): 85-88
- Berthevas P, Aguirre F, Tu J (2001) Recent developments in the recycling of flexible PU foams back into new PU foam products. *Proceedings of the Polyurethanes Expo 2001 Conference, Columbus, Ohio, USA*, pp 17-29
- Berthevas P, Santoro G, Wevers R, Gruenbauer H, Pizzi A (2005) Recycled polyurethane foam powder can be used in conjunction with PMDI in particle boards to obtain the required properties while reducing costs, *Proceedings 9th European Panel Products Symposium, Llandudno, UK*, pp 40-47
- Berthevas P, Villwock R, Martel B, Aguirre F (2004) Mobius PU recycling technology anf Dow's voranol and voractif polyols produce green slabstyoockfoams. *Proceedings 2004 Polyurethanes Conference, Las Vegas (Nevada), USA*
- Despres A, Pizzi A, Delmotte L (2006) ¹³C NMR investigation of the reaction in water of UF resins with blocked emulsified isocyanates, *J.Appl.Polymer Sci.*, 99(2): 589-596
- European Norm EN 312-5 and 7- Particleboard- Specifications (1999)
- Huntsman Polyurethanes (2006) Brochure: MDI/(M)UF hybrid systems in particleboard
 - Martel B, Villwock R, Stone H (2003) Polymeric foam powder processing techniques , *Foam Powder Products, and foams produced containing those foam powders. US patent 6,670,404 December 30 2003*
- Neuray MP, Wirth J, Sulzbach HM (2000) Methods for the recycling of polyurethanes, *Proceedings of the 2000 Polyurethane conference, Boston, Massachussetts, USA*, pp 37-48
 - Pichelin F (2006) private communication.
 - Pizzi A, Stephanou A (1993) On the chemistry, behaviour and cure acceleration of phenol-formaldehyde resins under very alkaline conditions, *J.Appl.Polymer Sci.*, 49, 2157-2160
- Pizzi A, Walton T (1992) Non-emulsifiable, water-based diisocyanate adhesives for exterior plywood, Part 1, *Holzforchung*, 46(6), 541-547

- Shutov F (1999) Recycling of polyurethane foam waste derived from used automotive seats. Proceedings of the 15th International Conference on Solid Waste Technology and Management. Philadelphia, PA, USA, pp 3D/1-3D/6
- Simon C, George B, Pizzi A (2002) Copolymerization in UF/pMDI adhesives networks, J.Appl.Polymer Sci., 86 (14): 3681 - 3688.
- Stone H, Villwock R, Martel B (2000) Recent technical advances in recycling of scrap polyurethane foam as finely ground powder in flexible foam, Proceedings of the 2000 Polyurethane conference, Boston, Massachusetts, USA, pp 3-10
- Wagner J, Peltzer K, Wirth J (1994) Process for powdering polyurethane, polycarbamide and/or polyurethane/polycarbamide materials in a rolling mill, Europea Patent EP 0711 331 B1
- Weigand E, Raschofer W, Hermann M, Baumann GF, Nakamura M (1993) Recycling polyurethanes put into practice. Proceedings Polyurethanes World Congress, Vancouver, BC, Canada, pp. 211-217
- Wieland S, Pizzi A, Hill S, Grigsby W, Pichelin F (2006) The reaction in water of UF resins with isocyanates at short curing times: a ¹³C NMR investigation, J.Appl.Polymer Sci., 100(2): 1624-1632
- You KK, Durocher DT, Kierkus PCH, Fishback TL (1997) Chemical recycling of polyurethanes and application of the recyclates, Proceedings Polyurethanes World Congress, Amsterdam, the Netherlands, pp. 598-692

Table 1. Results of plywood bonded with UF+PUR mix.

Wheat Flour (%)	PUR powder (%)	Dry Tensile strength (N/mm ²)	Tensile strength (min.)* 24h cold soak (N/mm ²)	5 min.	Resistance to boiling water (N/mm ²)			
					10min.	15 min.	20 min	
40 (control)	-	1.22	0	7.5	-	-	-	-
-	40	1.81	0.73	10	-	-	-	-
50(control)	-	1.54	0.88	9.5	0.84	0.0	-	-
-	50	1.86	1.09	13	-	-	-	-
20	20	2.04	1.30	12	-	-	-	-
25	25	2.02	1.03	12.5	-	-	-	-
10	30	1.85	1.30	16.5	1.21	0.80	0.51	0.0
10	40	2.26	1.47	17	1.36	0.93	0.66	0.0

* minutes taken to fall apart in boiling water

Table 2. Results of plywood bonded with PF+PUR mix.

Wood Flour (%)	PUR powder (%)	Dry Tensile strength (N/mm ²)	Tensile strength 24h cold soak (N/mm ²)	Tensile strength (N/mm ²)	Tensile strength 6h boiling (N/mm ²)
20	-	2.13		2.94	2.56
-	20	3.53		3.52	3.36

Table 3. Results of particleboard bonded with UF+PUR mix.

PF resin (%)	PUR powder (%)	Density (kg/m ³)	Dry IB strength (MPa)	IB strength after 6h boiling (MPa)	Thickness swelling (%)
9	-	690	0.54	0.18	12.2
8	1	690	0.61	0.23	8.3

7	2	690	0.53	0.28	8.6
6	3	690	0.15	0.0	-

FIGURE LEGENDS

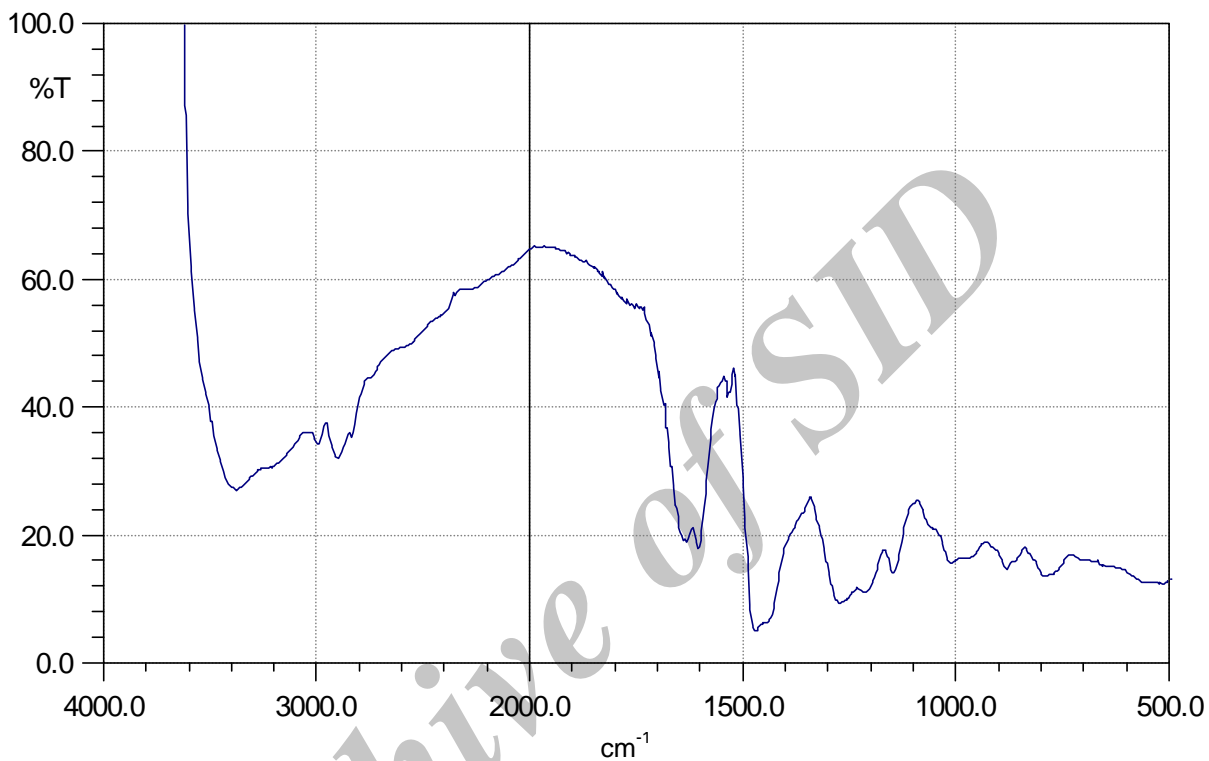


Fig. 1. FT-IR of hardened PF resin

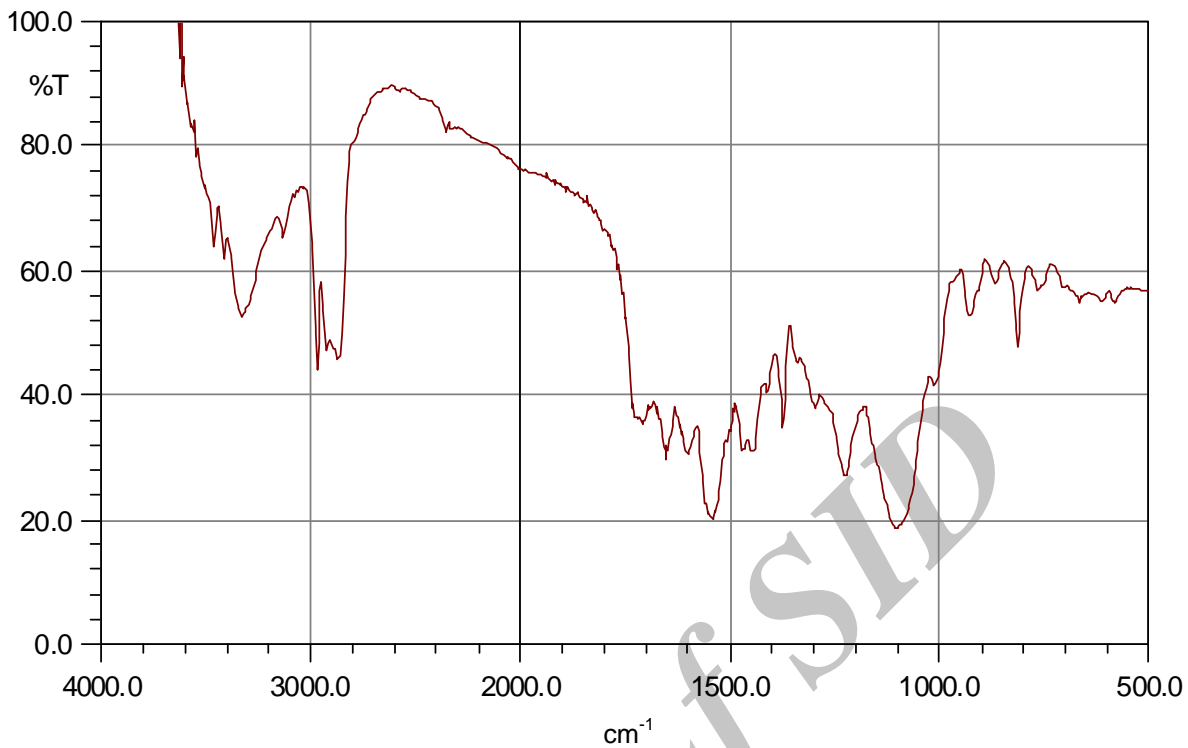


Fig. 2. FT-IR of micronized PUR nanopowder

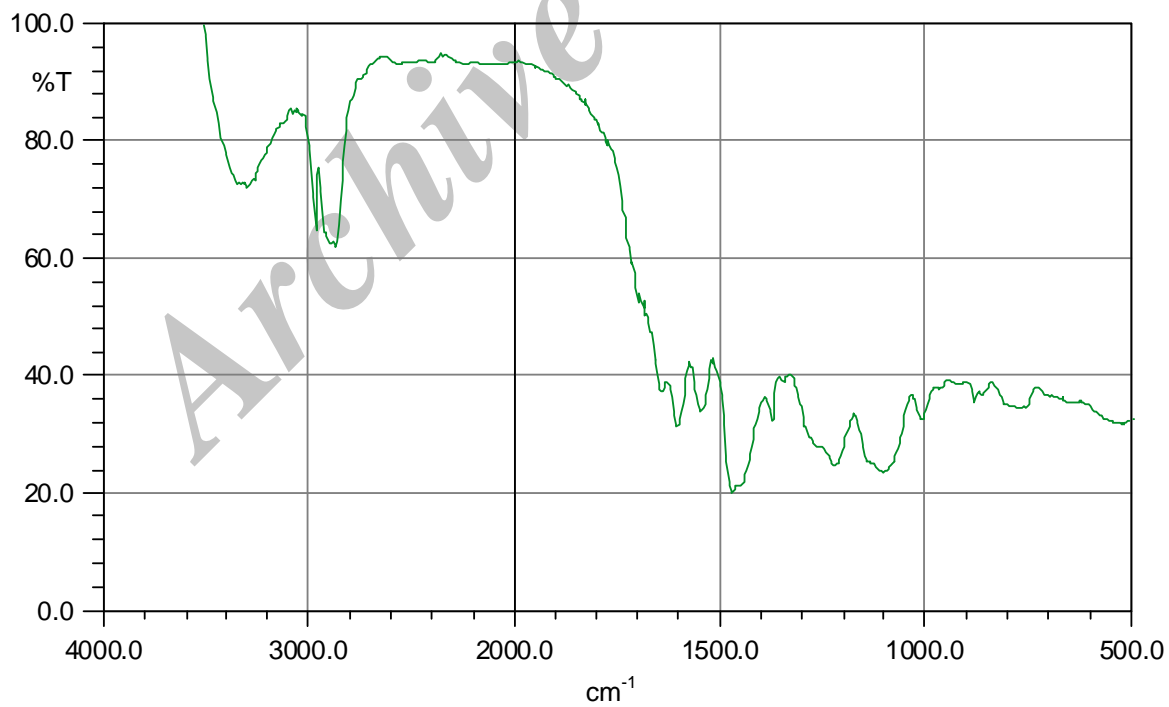


Fig. 3. FT-IR of hardened PF/PUR mix

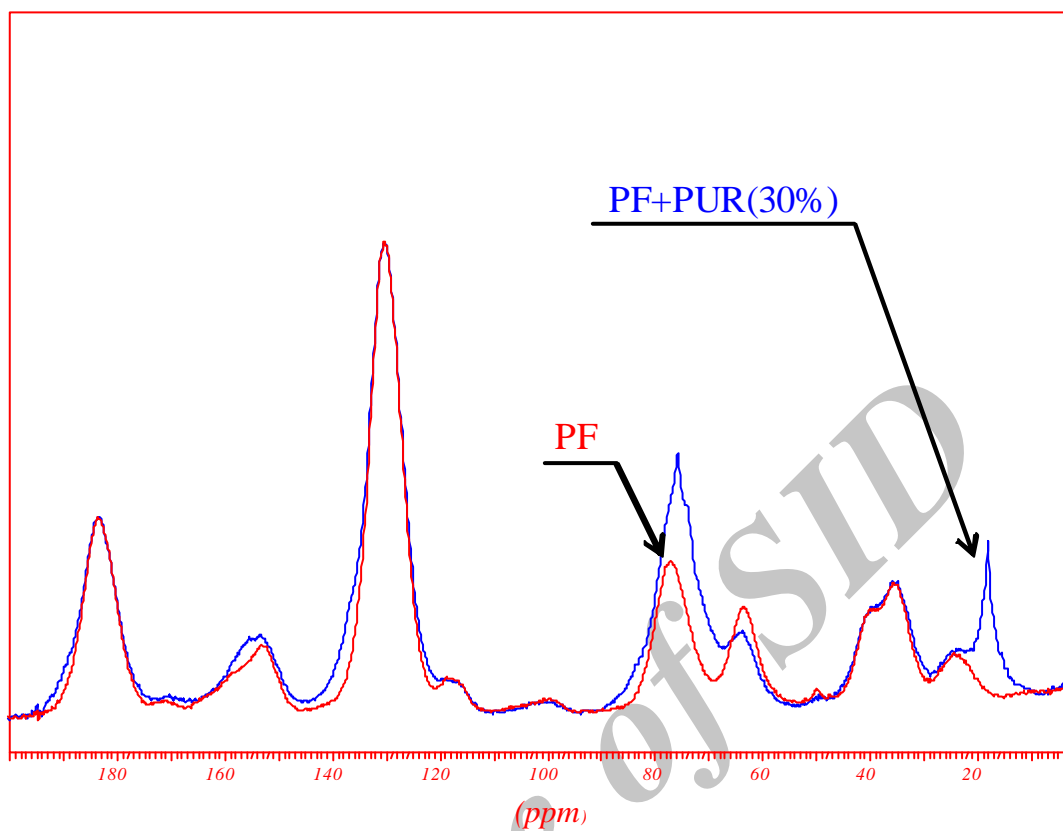


Fig. 4. Comparative solid phase CP-MAS ^{13}C NMR of hardened PF resin and of hardened PF/PUR mix

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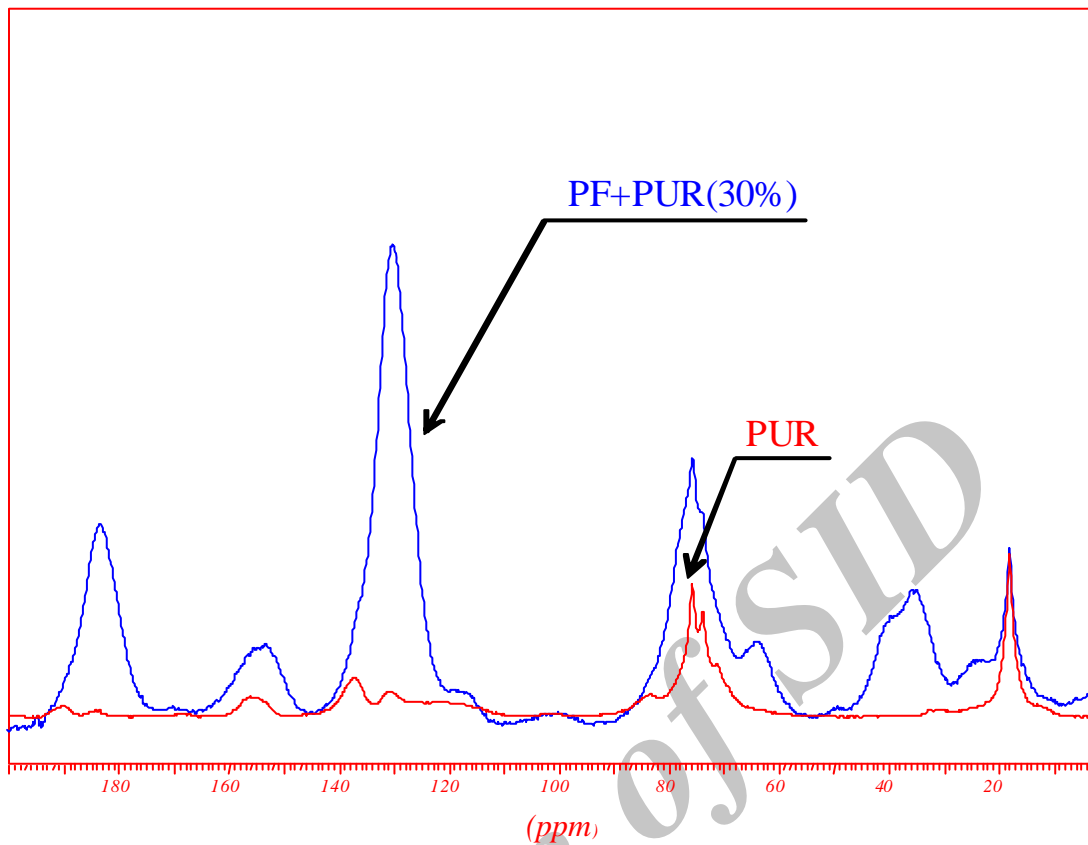


Fig. 5. Comparative solid phase CP-MAS ^{13}C NMR of hardened micromized PUR nanopowder and of hardened PF/PUR mix