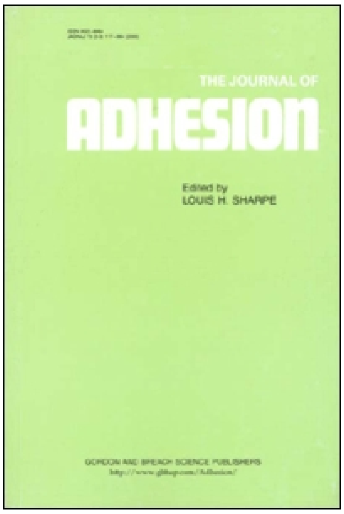
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Dynamic Mechanical Properties and Adhesive Joint Strengths of Emulsion Polymers Produced by Power Feed Technique. III. Adhesive Joint Strengths of Grafted Power Feed Copolymer

Hiroyuki Sumi[ab]; Akio Takemura[a]; Mikio Kajiyama[a]; Yasunori Hatano[a]; Bunichiro Tomita[a]; Hiroshi Mizumachi[a]
[a] Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Tokyo, Japan [b] Teijin Ltd, Sagamihara, Kanagawa, Japan

To cite this Article Sumi, Hiroyuki , Takemura, Akio , Kajiyama, Mikio , Hatano, Yasunori , Tomita, Bunichiro and Mizumachi, Hiroshi(1992) 'Dynamic Mechanical Properties and Adhesive Joint Strengths of Emulsion Polymers Produced by Power Feed Technique. III. Adhesive Joint Strengths of Grafted Power Feed Copolymer', The Journal of Adhesion, 38: 3, 173 — 184

To link to this Article: DOI: 10.1080/00218469208030453

URL: http://dx.doi.org/10.1080/00218469208030453

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1992, Vol. 38, pp. 173–184
Reprints available directly from the publisher
Photocopying permitted by license only
© 1992 Gordon and Breach Science Publishers S.A.
Printed in the United Kingdom

Downloaded At: 14:02 22 January 2011

Dynamic Mechanical Properties and Adhesive Joint Strengths of Emulsion Polymers Produced by Power Feed Technique. III. Adhesive Joint Strengths of Grafted Power Feed Copolymer*

HIROYUKI SUMI,** AKIO TAKEMURA,*** MIKIO KAJIYAMA, YASUNORI HATANO, BUNICHIRO TOMITA and HIROSHI MIZUMACHI

Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received August 28, 1991; in final form February 10, 1992)

Power feed copolymers were synthesized using styrene and n-butyl acrylate through non-uniform feeding emulsion polymerization. Poly(vinyl alcohol) (PVA) was used as a protective colloid, onto which vinyl monomers were grafted. Power feed copolymer had a very broad glass transition temperature compared with random copolymer, even if grafting and/or crosslinking were introduced to the system. This tendency was almost the same as the non-grafted power feed copolymer where only low molecular weight surfactant was used.

Adhesive joint strengths of power feed copolymers were evaluated compared with random copolymers. In the case of usual linear power feed copolymer, the adhesive joint strengths were not higher than those of random copolymer, which was considered to be due to the lower film strengths of the power feed copolymer. Power feed copolymer having grafting showed slightly higher adhesive joint strengths over a wide range of temperatures than random copolymer. When crosslinking was introduced to the system, power feed copolymer showed much higher adhesive joint strengths over a wide temperature range.

KEY WORDS power feed copolymer; broad transition; adhesive joint strengths; grafting; crosslinking.

INTRODUCTION

In the previous papers,[1-2] we have demonstrated the dynamic mechanical properties, chemical structure and adhesive joint strengths of power feed copolymer using n-butyl acrylate and styrene or methyl methacrylate. In the first of the previous papers,[1] it was shown that the power feed copolymer had a very broad glass transition temperature (Tg), and that Tg of the film cast from solution after breaking

---

*A part of this work was presented at the 40th Annual Meeting of the Japan Wood Research Society, 1990, Tsukuba, Japan.

**Present Address: Teijin Ltd. 3-37-19 Oyama, Sagamihara, Kanagawa 229, Japan.

***To whom correspondence should be addressed.

Downloaded At: 14:02 22 January 2011

down the emulsion was also very broad, which was considered to be due to the fact that power feed copolymers are composed of every possible combination of random copolymers. Further, it was shown that adhesive joint strengths of power feed copolymer were a little higher than those of random copolymers over a wide range of temperatures. The values themselves, however, were not very high. This was due to the poor cohesion between particles of the power feed copolymer which was a multicomponent system of random copolymers of various compositions.

In the second of the preceding papers,[2] we have explored the chemical structure and various factors in the synthesis of power feed copolymer using PVA (polyvinyl alcohol) as an emulsifier onto which grafting was introduced.

We have shown that adhesive joint strengths reach their maximum value around the glass transition temperatures of adhesive polymers.[3-14] Therefore, if we apply polymers having Tgs in a wide range of temperatures as adhesives, the adhesive joint strengths would be expected to show a high value in the corresponding temperature range.

In the present paper, we discuss the dynamic mechanical properties and adhesive joint strengths of power feed copolymers using PVA as an emulsifier onto which grafting was introduced. Grafting would be expected to increase the cohesion between phases of copolymers in power feed copolymer, which would lead to enhanced adhesive joint strengths. In order further to increase cohesion, polyisocyanate was added to introduce crosslinking to the system through the expected reaction between isocyanate groups and hydroxyl groups of PVA.

EXPERIMENTAL

Materials and Polymerization

The reagents used were styrene (St), n-butyl acrylate (nBA), ammonium persulfate (APS), and polyvinyl alcohol (PVA). Degrees of polymerization and of saponification of PVA were 1500 and 86.5–89.0 mole%, respectively. All the materials above were purchased from WAKO Chemicals Ltd. Aerosol OT (Nakarai Chemicals Ltd.) was used as the anionic surfactant. The water used was ion-exchanged. The crosslinking agent was a commercial MDI-Type polyisocyanate crosslinker AG (Koyo Sangyo).

The polymerization procedure was described in the previous papers.[1,2]

Measurement of Dynamic Viscoelasticity

Film specimens were made by casting from emulsion and drying at room temperature, followed by vacuum drying at 100°C for 8 hours. The dynamic viscoelasticity of the films was measured with a Rheovibron DDV-II (Toyo Baldwin Co.) in the temperature range of − 150°C to 150°C at a frequency of 110Hz with an approximate heating rate of 1°C/min.

Adhesive Joint Strengths

A cross-lap tensile testing method was used for these polymers, according to the design of Marra.[15-17] Adherends used were Birch (*Betula maximowicziana* Regel;

Japanese Kaba). The sizes of specimens and bonding areas were as follows: 6.5×2.5×2.5 cm, 6.25 cm^2. Emulsion polymers were directly applied to the bonding surface, then pressed at 10 kg/cm^2 for a day at 20°C and 65% RH. In the above case, a strong spring was inserted between the specimens and a clamp. When polyisocyanate was used, 5 phr of polyisocyanate was mixed with the emulsion before application to the bonding surface, then the specimens were pressed for a day at 20°C and 65% RH, and then placed in an oven of 70°C for 2 hours before releasing pressure. All specimens were conditioned at 20°C and 65% RH for one week before testing.

The adhesive joint strengths were measured with a Tensilon tensile testing machine (Toyo Baldwin Co.) equipped with a temperature controlled chamber, over the temperature range from −60°C to 60°C. The cross head speed was 10 mm/min. Temperature control was maintained by a combination of liquid nitrogen cooling and an electric heater.

Downloaded At: 14:02 22 January 2011

RESULTS AND DISCUSSION

Viscoelasticity

The polymers used here were the same as those of the preceding paper,[2] for which the polymerization recipe, grafting, molecular weight distributions, etc. are shown in Tables I and II.

Figure 1 shows the dynamic viscoelasticities of a typical power feed copolymer (A-1) and a random copolymer (A-2) without PVA, respectively. The loss modulus (E″) of the power feed copolymer shows a very broad peak in the temperature range between −20 and 40°C, while that of the random copolymer has a sharp peak at about 30°C. The storage modulus (E′) decreases gradually from −40°C as the temperature increases in the case of power feed copolymer.

TABLE I

Polymerization recipe and molecular weight distribution of synthesized emulsion polymers

No.	Far tank	Near tank	Feeding methods	PVA (g)	APS (g)	Aerosol OT (g)	Mn[d] (X10^{-3})	Mw[e] (X10^{-3})	d[f]
A-1	St	nBA	PF[b]	0	1.0	1.0	124	735	5.9
A-2	(St +	nBA)[a]	Ra[c]	0	1.0	1.0	121	667	5.5
C-1	St	nBA	PF	17.5	1.0	0	38	176	4.7
C-2	(St +	nBA)	Ra	17.5	1.0	0	36	167	4.7
C-4	St	nBA	PF	17.5	1.0	1.0	140	758	5.4
C-5	(St +	nBA)	Ra	17.5	1.0	1.0	101	524	5.2
C-6	nBA	St	PF	17.5	1.0	1.0	94	443	4.7

[a] Parenthesis means monomers were mixed previously
[b] Power feed polymerization
[c] Random polymerization
[d] Number Average Molecular Weight
[e] Weight Average Molecular Weight
[f] Polydispersity

Downloaded At: 14:02 22 January 2011

TABLE II
Grafting and conversion of emulsion polymers

No.	Far tank	Near tank	Feeding methods	Polymer content	Total conversion	Grafting	Grafting efficiency	Grafting efficiency of backbone polymer
A-1	St	nBA	PF	33.5	98.0	—	—	—
A-2	(St +	nBA)	Ra	33.7	98.6	—	—	—
C-1	St	nBA	PF	32.2	91.3	688	36.5	51.0
C-2	(St +	nBA)	Ra	32.3	91.4	606	32.1	60.2
C-4	St	nBA	PF	33.7	95.7	630	32.0	45.7
C-5	(St +	nBA)	Ra	34.6	98.1	683	33.5	48.8
C-6	nBA	St	PF	33.9	96.3	777	39.2	45.9

Figure 2 shows the dynamic mechanical data for the system in the presence of PVA (C-1 and C-2), where E′ and E″ have shifted to a higher temperature. The transition around 95°C could be derived from the crystalline PVA. The transition temperature became higher and the transition width became broader. But in these systems, the broad peaks were observed in an "M" shape. This fact is considered to be due to the polymer system having a phase-separated morphology composed

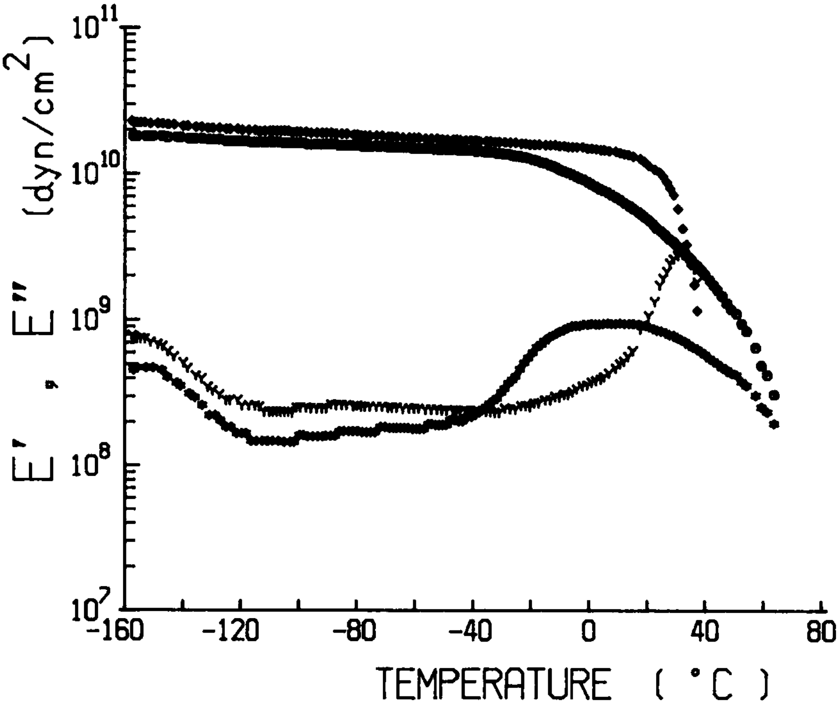


FIGURE 1 Temperature Dependencies of Dynamic Mechanical Moduli for Power Feed Copolymer (○ *) and random copolymer (◇ Y) without PVA.

Downloaded At: 14:02 22 January 2011

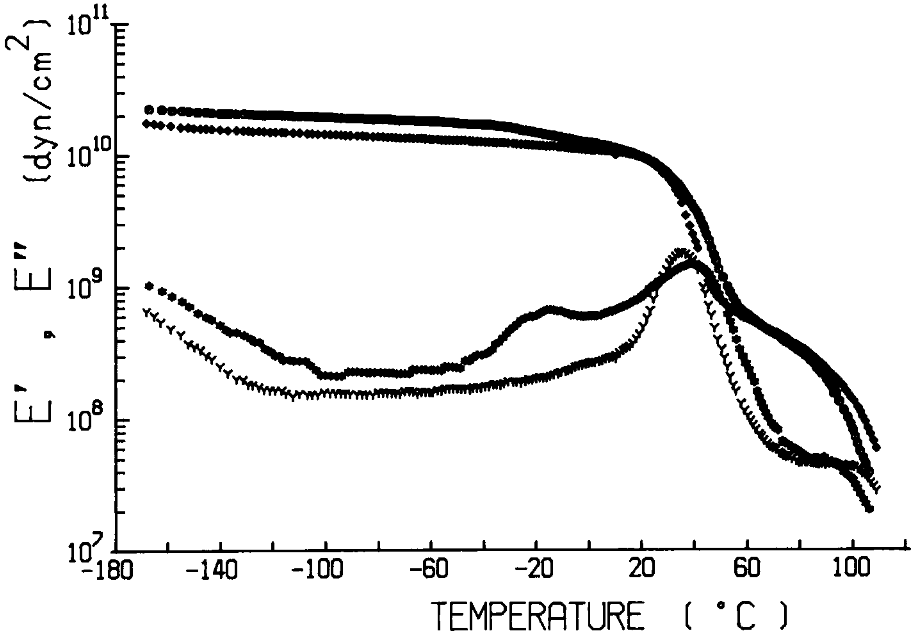


FIGURE 2 Temperature Dependencies of Dynamic Mechanical Moduli for Power Feed Copolymer (O *) and random copolymer (◇ Y) with PVA.

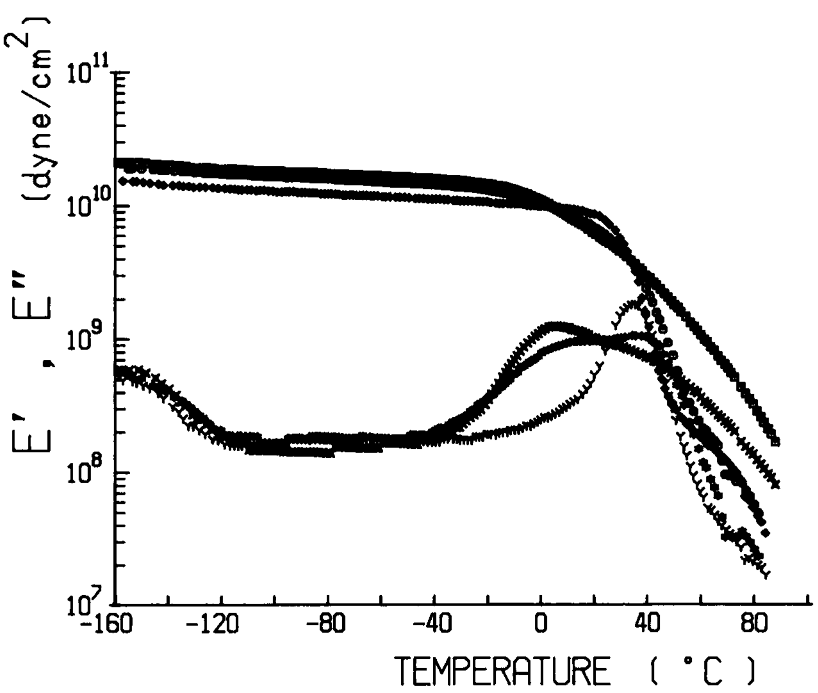


FIGURE 3 Temperature Dependencies of Dynamic Mechanical Moduli for Power Feed Copolymer with St Far and nBA Near Tank (O *), power feed copolymer with nba far and st near tank (☐ X) and Random Copolymer (◇ Y) with Both PVA and Surfactant.

of PSt-rich phase and P(nBA)-rich phase to some degree. Figure 3 shows the temperature dependencies of the dynamic moduli for the system using PVA combined with surfactants (C-4, C-5 and C-6). Here, an "M" shape transition was not observed, and the transitions of PVA were barely detected around 80°C, which is 20°C lower than the system in Figure 2. This fact is considered to be due to the low molecular weight surfactant preventing the phase separation from occurring between PVA and copolymers.

Figure 4 shows the dynamic mechanical data for the emulsion polymers C-4 and C-5 cured with polyisocyanate crosslinking agent. The dynamic moduli were almost the same as those of linear polymers which were synthesized without PVA. However, in the higher temperature range, the dynamic storage moduli of power feed copolymer and random copolymer did not drop off as rapidly as did those of the linear polymers, which were in the rubbery plateau region. According to the kinetic theory of rubber elasticity,[18] the modulus E′ can be approximated as follows;

$$E' = nRT$$

where n is the number of network segments in a unit volume, R is the gas constant and T is the temperature. The moduli of the random copolymer and the power feed copolymer were almost equal in the higher temperature region, so n is considered to be the same in both cases. It is well known that n is proportional to the crosslinking density. Therefore, there would be no large difference in crosslinking density between random copolymer and power feed copolymer in this case.

Downloaded At: 14:02 22 January 2011

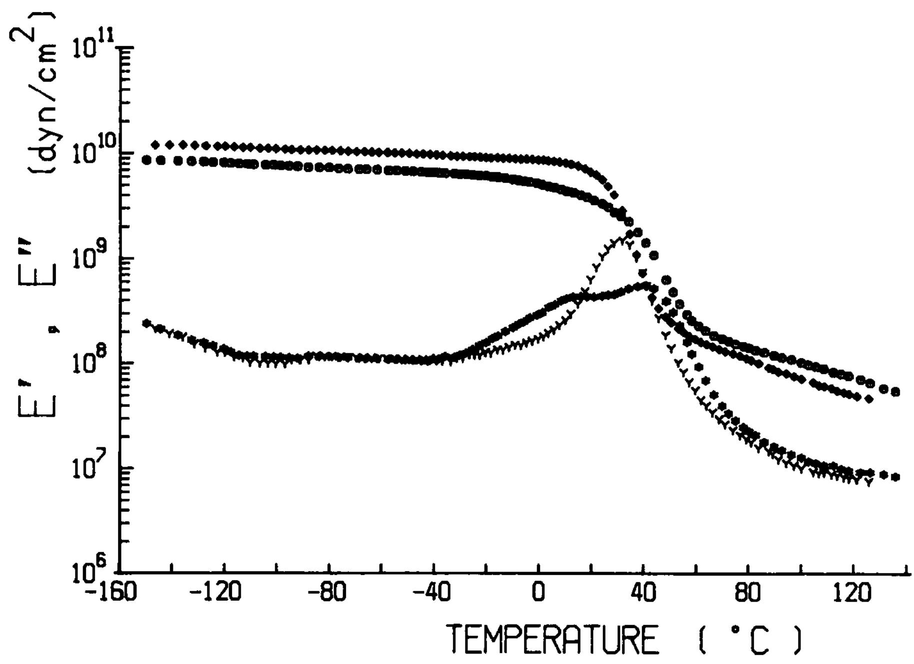


FIGURE 4 Temperature Dependencies of Dynamic Mechanical Moduli for Crosslinked Power Feed Copolymer (○ *) and random copolymer (◇ Y) with Both PVA and Surfactant.

Downloaded At: 14:02 22 January 2011

Adhesive Joint Strengths

Figures 5 and 6 show the temperature dependencies of adhesive cross-lap tensile strengths for power feed copolymer and random copolymer grafted onto PVA, respectively. The maximum adhesive joint strengths were observed around the Tgs of both the power feed and random copolymers. In the case of the random copolymer, adhesive joint strengths showed a sharp peak just around Tg, the shape of which is exactly similar to that of loss modulus (E″). On the other hand, the adhesive joint strengths of the power feed copolymer were higher than those of the random copolymer between the temperatures of −10 and 30°C. The adhesive joint strengths can be said to be broad, just as the material's E″ is. Wood failure was almost the same for both polymers. The analysis of variance for the PVA system is shown in Table III. No significant difference is observed between −50 and 50°C. However, between −10 and 0°C, Fo is 7.5, which means that the power feed effect is significant at the 5% level.

Figures 7 and 8 show the temperature dependencies of adhesive cross-lap tensile strengths for power feed copolymer and random copolymer grafted onto PVA in the presence of surfactant, respectively. From the dynamic mechanical data, these systems are less phase separated than systems with PVA alone. The adhesive joint strengths, however, were not similar to the E″, and were not very high. The low molecular weight surfactant is responsible for the reduced adhesive joint strengths.

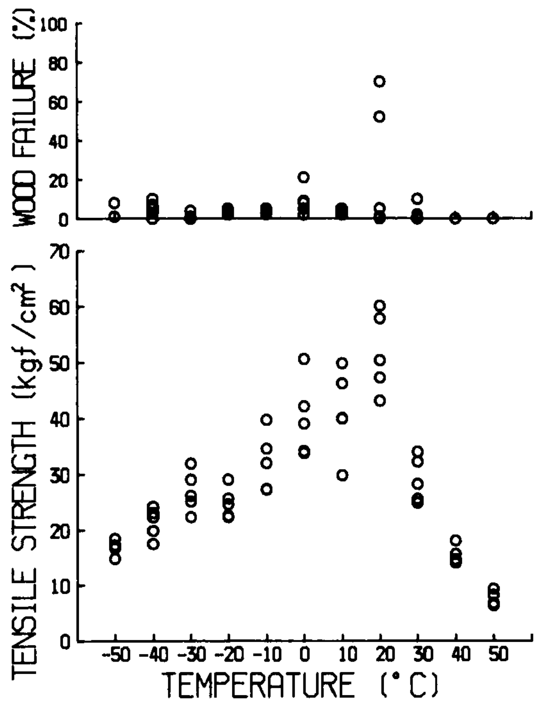


FIGURE 5 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Power Feed Copolymer Grafted onto PVA.

Downloaded At: 14:02 22 January 2011

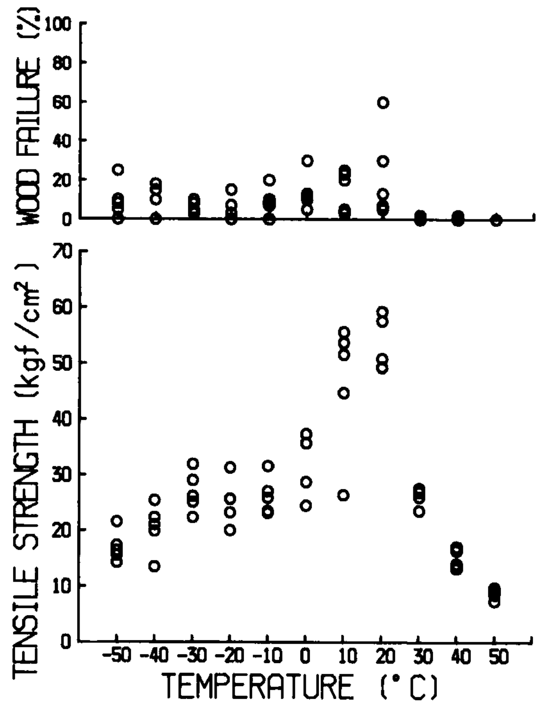


FIGURE 6 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Random Copolymer Grafted onto PVA.

TABLE III
Analysis of variance for adhesive joint strengths of polymers grafted onto PVA

Source of variation	Sum of squares	Degrees of freedom	Mean squares	Fo
A : Temperature	16592.1735	10	1659.2174	71.8452
B : Polymer	17.7042	1	17.7042	0.7666
A X B	302.8277	10	30.2828	1.3113
Error	2032.3021	88	23.0943	
Total	18945.0075	109		

Before experimenting with the polyisocyanate systems, adhesive joint strengths were determined at room temperature using different amounts of crosslinking agent. According to that study, 10 phr of polyisocyanate in the emulsion polymers gave the highest adhesive joint strengths; however, 5 phr addition was adopted, for which the adhesive joint strengths were a little lower than those of the 10 phr system. Usually, crosslinking broadens the Tg of polymers. Using less crosslinking agent was considered to be better in this respect, therefore 5 phr was adopted. Figures 9 and 10 show the temperature dependencies of adhesive cross-lap tensile strengths for power feed copolymer and random copolymer, grafted onto PVA in the presence of surfactant and crosslinked by polyisocyanate, respectively. In the case of the random copolymer, the adhesive joint strengths became maximum at 30°C,

Downloaded At: 14:02 22 January 2011

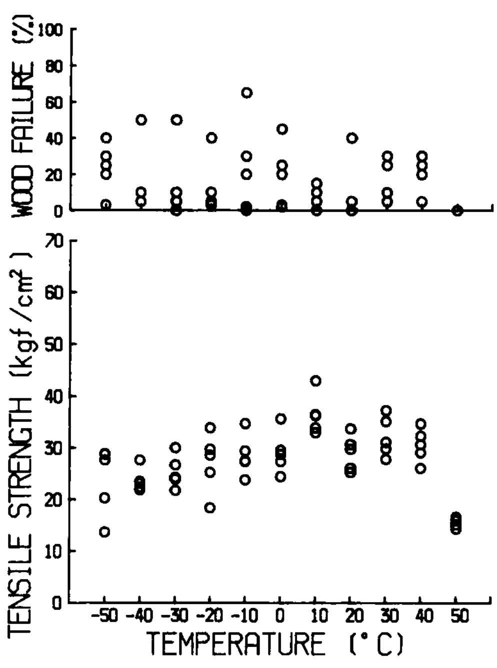


FIGURE 7 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Power Feed Copolymer Grafted onto PVA with Anionic Surfactant.

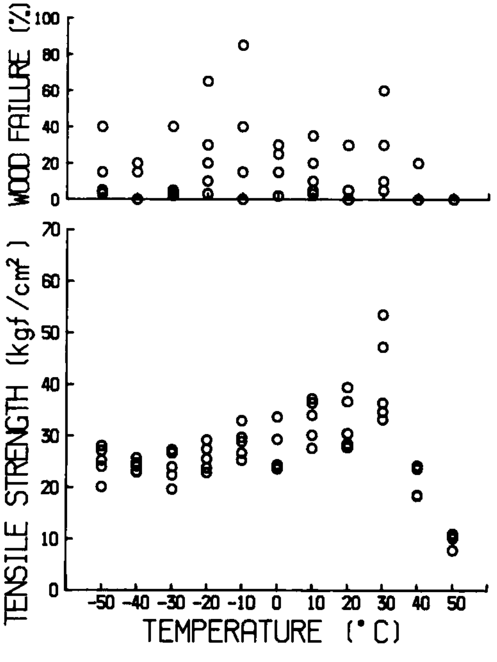


FIGURE 8 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Random Copolymer Grafted onto PVA with Anionic Surfactant.

Downloaded At: 14:02 22 January 2011

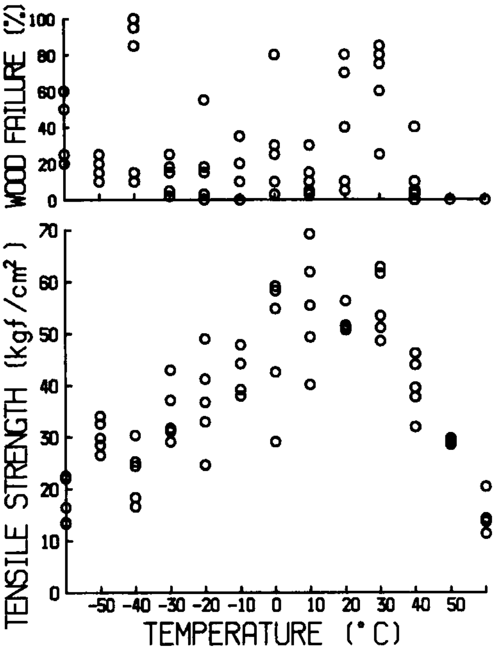


FIGURE 9 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Power Feed Copolymer Crosslinked with Polyisocyanate as Well as Grafted onto PVA.

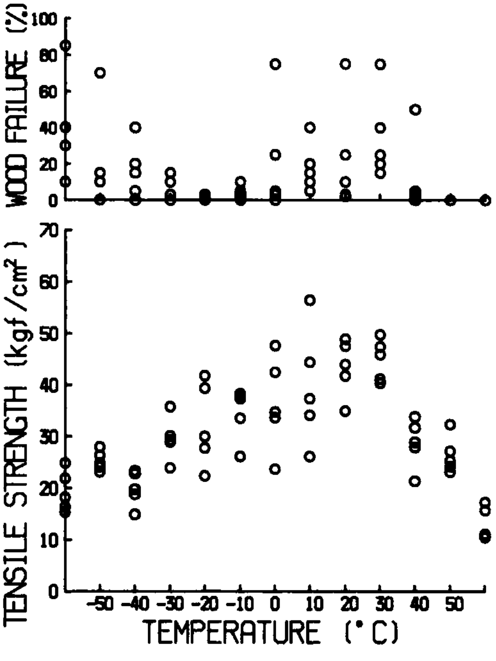


FIGURE 10 Temperature Dependencies of Adhesive Cross-lap Tensile Strengths for Random Copolymer Crosslinked with Polyisocyanate as Well as Grafted onto PVA.

Downloaded At: 14:02 22 January 2011

which coincided with the E″ of the polymer. On the other hand, the power feed copolymer had higher adhesive joint strengths than the random copolymer over the whole temperature range. Especially, the adhesive joint strength of the power feed copolymer was maintained over the broader temperature range of −10 and 40°C. Furthermore, the adhesive joint strength for the crosslinked power feed copolymer was highest among all of the other power feed copolymers that were synthesized. With regard to wood failure, crosslinked systems had higher values than non-crosslinked systems. As mentioned in the section on dynamic mechanical properties, the crosslinking density of the power feed and random copolymers were almost the same, so it is reasonable to omit this factor in a comparison of adhesive joint strengths. Consequently, it can be concluded that the broad adhesive joint strengths of power feed copolymer were due to the broad transition in the polymer. In order to confirm the results, two-way classification method was applied. The analysis of variance for the PVA/crosslinked system is shown in Table IV. It is known that the F_0 of the variation B, which is the effect of the difference of polymers, is large enough to be recognized at 1% level over the whole temperature range.

It is assumed that the polyisocyanate crosslinker reacted with hydroxyl groups of PVA, which caused a tight cohesion between the phases which otherwise would have separated, and that adhesive joint strength was greatly improved thereby.

CONCLUSIONS

Power feed copolymer had a very broad Tg over a wide range of temperature compared with random copolymer, even if crosslinking and/or grafting were introduced to the system. This tendency was almost the same for the non-grafted power feed copolymer where only low molecular weight surfactant was used.

Adhesive joint strengths of power feed copolymers were evaluated and compared with random copolymer. In the case of the usual linear emulsion copolymers, power feed copolymer did not show higher adhesive joint strengths than those of random copolymer. This was attributed to the lower cohesion strengths of the power feed copolymer. Power feed copolymers with grafting showed slightly higher adhesive joint strengths over a wide range of temperatures than random copolymer. When crosslinking was introduced, power feed copolymer showed much higher adhesive joint strengths over a wide temperature range than random copolymer. These facts

TABLE IV
Analysis of variance for adhesive joint strengths of polymers grafted onto PVA crosslinked with isocyanate

Source of variation	Sum of squares	Degrees of freedom	Mean squares	Fo
A : Temperature	628136.6109	12	52344.7176	34.1087
B : Polymer	53876.6327	1	53876.6327	35.1069
A X B	27683.9423	12	2306.9952	1.5033
Error	159602.9040	104	1534.6433	
Total	869300.0899	129		

were confirmed by an analysis of variance. It is concluded that power feed copolymer has a great potential for application as an adhesive to be used in places where cold and warm weather alternate. The material should provide joints which are durable against various stresses, such as peeling or shear.

Acknowledgement

A part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

References

1. A. Takemura, K. Shimizu, B. Tomita, and H. Mizumachi, *J. Adhesion*, **37,** 161 (1992).
2. H. Sumi, A. Takemura, B. Tomita, and H. Mizumachi, *J. Adhesion*, this issue (1992).
3. H. Mizumachi, M. Tsukiji, Y. Konishi, and A. Tsujita, *J. Adhesion Soc. Japan.*, **12,** 378 (1976).
4. H. Mizumachi, Y. Hatano, K. Kamei, and Y. Yamagishi, *Mokuzai Gakkaishi*, **25,** 288–295 (1979).
5. H. Mizumachi, Y. Hatano, and Y. Yamagishi, *Holzforschung*, **34,** 169 (1980).
6. Y. Hatano, B. Tomita, and H. Mizumachi, *Mokuzai Gakkaishi*, **29,** 578 (1983).
7. K. Motohashi, B. Tomita, H. Mizumachi, and H. Sakaguchi, *Wood and Fiber Sci.*, **16**(1), 72 (1984).
8. K. Motohashi, B. Tomita, and H. Mizumachi, *Holzforschung*, **36,** 183 (1982).
9. K. Motohashi and B. Tomita, *Mokuzai Gakkaishi*, **25,** 225–232 (1979).
10. A. Takemura, B. Tomita, and H. Mizumachi, *J. Appl. Polym. Sci.*, **30,** 4031 (1985).
11. A. Takemura, K. Shiozawa, B. Tomita, and H. Mizumachi, *ibid.*, **31,** 1351 (1986).
12. A. Takemura, H. Kurikyama, T. Moriguchi, B. Tomita, and H. Mizumachi, *Mokuzai Gakkaishi*, **32,** 813 (1986).
13. A. Takemura, B. Tomita, and H. Mizumachi, *ibid.*, **32,** 883 (1986).
14. Y. Hatano, B. Tomita, and H. Mizumachi, *Holzforschung*, **40,** 255 (1986).
15. A. A. Marra, *Forest Products J.*, **5,** 301 (1955).
16. A. A. Marra, *ibid.*, **5,** 385 (1955).
17. A. A. Marra, *ibid.*, **6,** 142 (1956).
18. S. Murahashi and H. Tani, *Kobunshikagaku* (Ryoritsu Publishing Co., 1974), p. 277–279.

Downloaded At: 14:02 22 January 2011