Effect of Curing Agent on Interfacial Adhesion in Acrylic Polymer-Based Laminates

J. WOOTTHIKANOKKHAN, R. P. BURFORD, R. P. CHAPLIN

Department of Polymer Science, School of Chemical Engineering and Industrial Chemistry,
University of New South Wales, New South Wales 2052, Australia

ABSTRACT: The effect of crosslinking on interfacial adhesion between an acrylic elastomer and poly(methyl methacrylate) has been studied using a 90° peel test. Elastomers were master-batched with a 1 : 10 sulfur/sodium mixture. The compounded elastomer was then bonded with poly(methyl methacrylate) by *in situ* curing at various temperatures. Variations in the curing affect both the mechanism of adhesion and separation. The relationship between peel strength and crosslink density is found to be $P = kM_c$. Crosslinking at relatively low temperatures produced a partially crosslinked elastomer that leads to high peel strengths. When crosslinked at 180°C, the acrylic elastomer was completely cured, and the peel strength decreased by more than 80%. This is consistent with an optimum level of crosslinking required for peel strength. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1277–1284, 1998

Key words: acrylic rubber; acrylic elastomer curing; adhesion; poly(methyl methacrylate); peel test

INTRODUCTION

Consider a system comprising a soft polymer A, a rigid polymer B, and an interfacial region C. The combined strength of the system in a peel test not only depends on the strength of the interface, but also on the inherent properties of the constituent polymer. Gent and Hamed,[1] in particular, illustrate this by considering an energy balance for detachment of unit area during steady-state peeling. Here, the work required to break an interference is regarded as the sum of two main contributions. One is the thermodynamic surface energy, which is associated with either a chemical or physical interaction across the interface. This term is independent of separation rate and thickness of the material making up the joint. How-

ever, in practice, it is usually found that the energy required to break the interface is several orders of magnitude larger than the surface energy. A rate dependence is also exhibited. The greater energy to break is attributed to the other contribution (i.e., mechanical energy dissipated by irreversible deformation processes of the material making up the joint, around the crack front).

The relationship between cohesive and adhesion strength of elastomers has been previously studied and discussed by Hamed and Shieh.[2] For example, a study of self-adhesion in styrene butadiene rubber (SBR) rubber showed that, after the two elastomeric layers are brought into contact, the interface eventually disappeared. Tack strength (defined as an ability to resist separation after contacting under reasonably low pressure for a short time) increased with time and reached equilibrium. The tack becomes identical to the cohesive strength of material.

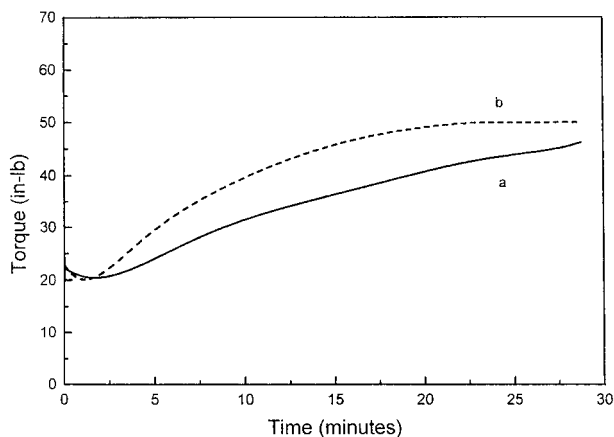Studies of various elastomers[3] show that tack

Figure 1 Overlaid rheographs of acrylic rubber with 4% (a) and 8% (b) sulfur at 180°C.

can be changed if the viscoelastic response of the elastomer is also changed. For example, by varying the testing rate, the viscoelastic behavior of the elastomer changed from viscous-flow to more elastic behavior. Stress concentration at the fracture front increased, lowering tack. For high tack, an elastomer should have a low viscosity to facilitate bond formation, but a high cohesive strength at high strain to resist bond separation.

In developing elastomeric adhesives, the most direct way of controlling performance is by adhesive modification, including curing. The effects of crosslinking on adhesion properties of an elastomer have been extensively studied. For example, Zosel[4] suggested that crosslinking affects both bond formation and separation, with these effects being contradictory in mode of action.

Crosslinking influences a range of elastomer properties including modulus, hardness, toughness, tear strength, and tensile strength.[5] The modulus and hardness increased linearly with crosslink density, whereas properties related to energy to break (such as tear strength and toughness) increase with small amounts of crosslinks, but are reduced with increasing crosslink density. These changes led to a greater amount of energy being required to deform the adhesive during separation. The effect of crosslinking on the mechanical properties of acrylic adhesives is reported by Dale and colleagues.[6] Tensile strength increases with an increase in crosslinker content by up to twenty times. The results of dynamic testing also show a large increase in the storage modulus, with an increasing amount of crosslinker.

Increasing interfacial interaction via cross-

linking across the interface also improves adhesion.[7] Two partially crosslinked elastomers were pressed together and curing then taken to completion. Adhesion strength increased linearly as the amount of crosslinking between the two sheets was increased.

On the other hand, crosslinking decreased the segmental mobility of adhesive molecules responsible for intimate contact and interdiffusion across the interface. Zosel[8] studied the effect of crosslinking on the strength of poly(butyl methacrylate) latex film. The result shows that films from highly crosslinked particles remain brittle upon annealing. This is because interdiffusion and the formation of interparticular entanglements are impossible in these latex films. Druschke[9] has investigated the effect of crosslinking on adhesion for a low molecular weight acrylic solution polymer. The result shows that peel adhesion decreased by 35% with the use of 1% crosslinking agent. It is generally believed that the material will possess an optimum balance between good deformability and high strength at some ideal extent of crosslinking.

The present work has centered on the study of interfacial adhesion in acrylic polymers. Specifically, it has focused on adhesive application to a rigid thermoplastic substrate to provide laminates that form the basis of many applications, including retroreflective sheeting. The claimed sheet is used for highway signs and advertising boards, and comprises a clear plastic layer lying over a base sheet, which contains glass microspheres or other retroreflective elements. The cover sheet protects the base sheet, including the retroreflective elements, from
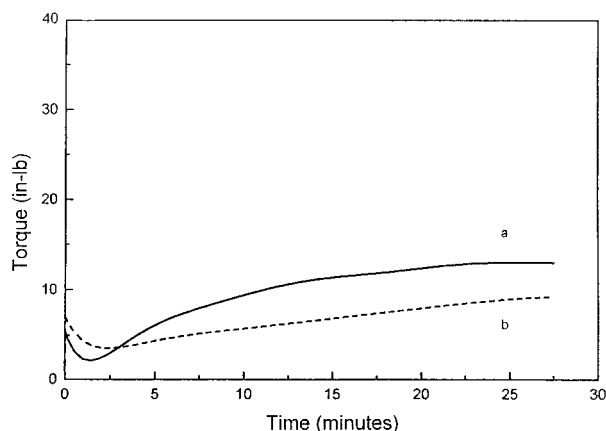

Figure 2 Overlaid rheographs of acrylic rubber with 1% sulfur at 180°C (a) and 140°C (b).
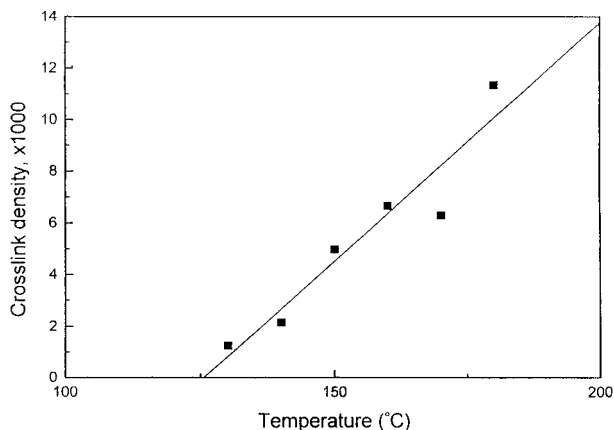
Figure 3 Change of crosslink density of acrylic rubber as a function of cure temperature.

Figure 5 Change of control peel strength with temperature.

water droplets that can affect the optics of the lenses when exposed to rain. It is important to ensure good adhesion between the cover sheet and the reflective element embedded in the binder layer for durability. The relevant patent literature[10] reveals that an acrylic binder, capable of undergoing *in situ* radiation curing, was used as the adhesive. This leads to a great improvement in adhesion between poly(methyl methacrylate)(PMMA) and the base sheet.

Most commercial acrylic elastomers have a small percentage (typically 1–5%) of reactive cure sites, such as epoxy, hydroxy, and chlorine groups.[11] The chlorine type, which can be crosslinked with various cure systems (including soap/ sulfur, soap/amine, thiourea, polyamine, and diamine) is most commonly used, and sodium or potassium stearate soap is the most common
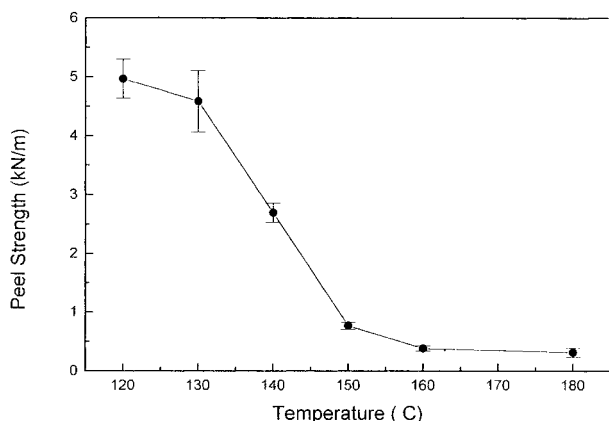
crosslinker. It functions as the primary curative or acceptor of the released chlorine, whereas the sulfur acts as an accelerator. The crosslinks are of the polysulfide type. Curing is usually performed at a 10 : 1 weight ratio of soap/sulfur, over a temperature range from 150°C to 180°C.[12]

In this article, the curing behavior of an acrylic elastomer was studied and data correlated with the adhesion properties of the system. The aim was to investigate the effect of crosslinking on the mechanism of adhesion and separation in the laminate system.

EXPERIMENTAL

A simple laminate joint was used as a model. Adhesion was measured by mechanical testing, with the fracture surface and separation behavior be-
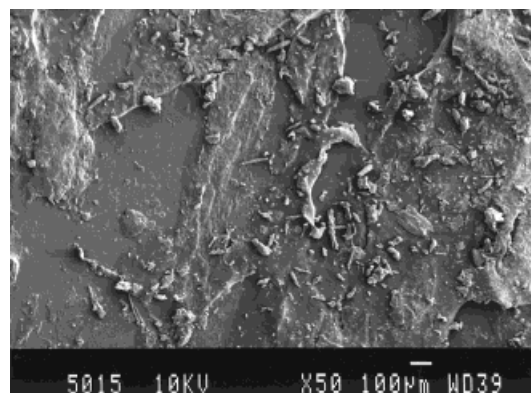

Figure 4 Change in peel strength with curing temperature.

Figure 6 Scanning electron micrographs of PMMA peeled surface after *in situ* curing at 130°C.
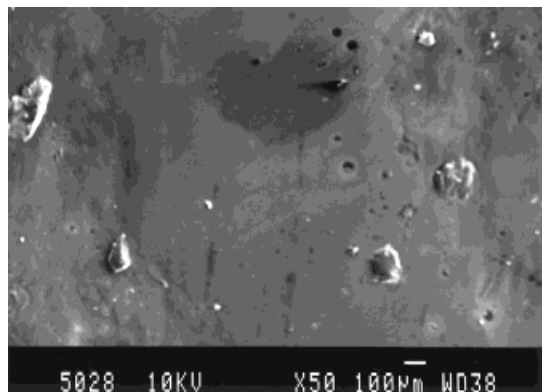
Figure 7 Scanning electron micrographs of PMMA peeled surface after *in situ* curing at 180°C.

ing recorded micro- and macroscopically. Because both cure rate and interdiffusion are temperature-dependent, the effect of crosslinking on the adhesion was studied by following changes in adhesion strength as the laminate joint was cured *in situ* at various temperatures. A system in which the crosslinking agent was absent was also examined as a control.

Sample Preparation

HYTEMP 4051CG acrylic elastomer [containing mainly poly(ethyl acrylate)] was obtained from GEON Australia Pty. Ltd. and has a T_g of ≈ -11°C. Thermal curable rubber was prepared by mixing sulfur and sodium stearate (1/10, w/w) with the rubber, at various compositions, in a "Haake" 600 internal mixer of 60 cm^3 chamber capacity and with Banbury-type rotor blades. The mixing was performed at 60 rpm for 10 min at 65°C. The compounded rubber was then compression-molded into 3 mm thick sheets.

The cure behavior of the elastomer was measured using a Monsanto Model MP_V oscillating-disk rheometer in general accordance with ASTM D-2084. A biconical disk is oscillated through a rotational amplitude of 1°C with a standard frequency of 100 cpm (1.7 Hz).

The extent of cross-linking was determined from equilibrium swelling measurements. Duplicate pieces ~ 1 cm^2 were carefully weighed (± 1 mg) and reweighed after swelling to equilibrium weight (1 week) in methyl ethyl ketone (MEK). The crosslink density was calculated from the Flory-Rehner equation.

$$\nu = -[\ln(1 - V_r) - V_r + x(V_r)^2]/V_s(V_r)^{1/3} \quad (1)$$

where V_r is volume fraction of the polymer in swollen gel,

$$V_r = V_d/(V_d + V_s) \quad (2)$$

V_s is volume of solvent in rubber, V_d is volume of dry polymer, x is polymer–solvent interaction parameter, and ν is crosslink density.

The density of acrylic rubber and MEK used in the calculations is 1.1 and 0.8, respectively.

$$x \text{ for acrylic rubber/MEK}$$
$$\text{interaction} = 0.36.[13]$$

Adhesion Testing

Elastomeric strips (1.24 cm wide) cut from a 3-mm-thick molded sheet were used after reinforcement with fabric, which eliminates a viscoelastic contribution. The 3-mm-thick PMMA sheets used as substrate were machined to the appropriate test dimensions.

Fresh surfaces of each substrate were brought into contact, using a "Stacey" hydraulic press at 200 kPa, at temperatures ranging between 90°C to 180°C for 30 min. Each laminate was cooled to room temperature before testing within 24 h. The adhesion strength of the laminate joints was determined by a 90°C peel test, in accordance with the Pressure Sensitive Tape Council method (PSTC 14),[14] using an Instron 1115 universal testing machine and a crosshead speed of 5 mm
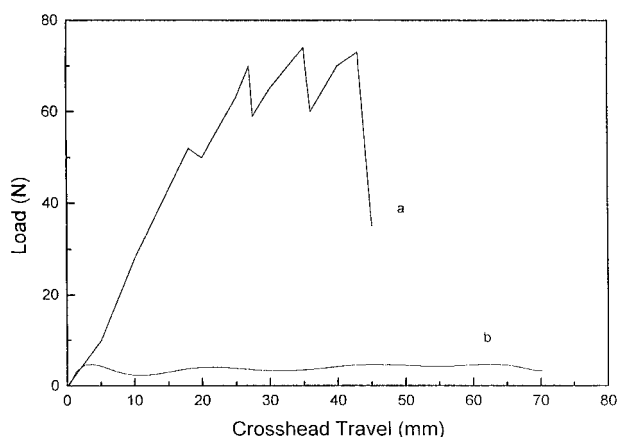

Figure 8 Overlaid force-displacement traces of the system at 130°C (a) and 180°C (b).
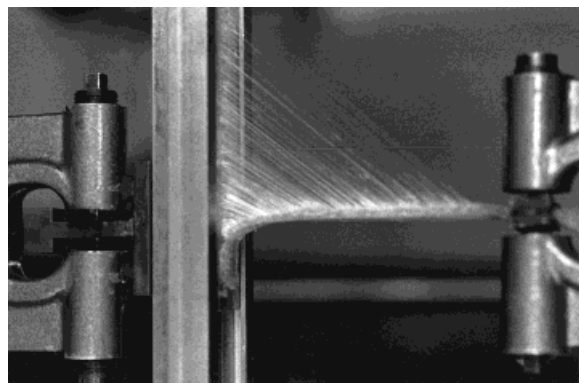
Figure 9 Peeling behavior of the control.

min^{-1}. Values are the average of five replicate experiments.

RESULTS AND DISCUSSION

Figures 1 and 2 show the curing behavior of the acrylic elastomer. It can be seen that torque decreases during the induction period, with a scorching time of ~ 2 min. As crosslinking takes place, the torque gradually increased, indicating the scorchy and slow curing nature of acrylic elastomers generally.[15] Figure 1 shows how the curing agent content affects the rate of curing. At 4% sulfur, the torque gradually increased and reaches a maximum torque at 45 lb-inch within 30 min, whereas with 8% curing agent, the rubber reaches a plateau after 30 min with a maximum torque of 50 inches-lb. The trend of an increase of cure rate with increasing level of curing agent agrees with that previously predicted by Brydson.[16]

Curing temperature also has an effect, as shown in Figure 2 for the acrylic elastomer with 1% sulfur. At 140°C, the torque increases very slowly; thus curing is incomplete after 30 min. At the higher temperature (180°C; Fig. 2, trace a), curing is faster and the torque has reached a plateau with a maximum at 12 inches-lb after 30 min, reflecting complete curing.

The effect of temperature on cure rate agrees with that previously discussed by Wise,[17] where the rate of cure doubles for every 10°C increase in temperature. A similar trend has also been reported for tetrafluoroethylene-propylene elastomers.[18]

The effect of temperature on the extent of cross-

linking is also reflected by equilibrium swelling (Fig. 3). Crosslink density increases linearly with increases in curing temperature.

Changes in peel strength with curing temperature are shown in Figure 4. At low temperatures, peel strength is higher than the control (Fig. 5), but decreased remarkably above 130°C, whereas the control changed little. These changes in interfacial adhesion are also reflected in surface topography. Scanning electron micrographs of the peeled PMMA surface are compared for the two extremes [i.e., at curing temperatures of 130°C (Fig. 6) and 180°C (Fig. 7)]. A micrograph of the joint bonded at a relatively low temperature shows residues of the elastomer on the PMMA substrate after peeling, reflecting good adhesion and cohesive failure. The corresponding peel force-displacement trace [Fig. 8(a)] shows an increase to a rather high load (75 N) before sample separation. The trace shows stick-slip behavior, also reflecting good adhesion and cohesive failure.

At the higher curing temperature, a relatively clean PMMA surface results; thus, failure mode is at the interface. This reflects poor adhesion. The force-displacement [Fig. 8(b)] indicates that force is very low (≈ 5 N), and a less pronounced stick-slip behavior is exhibited.

The effect of crosslinking on adhesion can be explained in the following way. Crosslinking in-
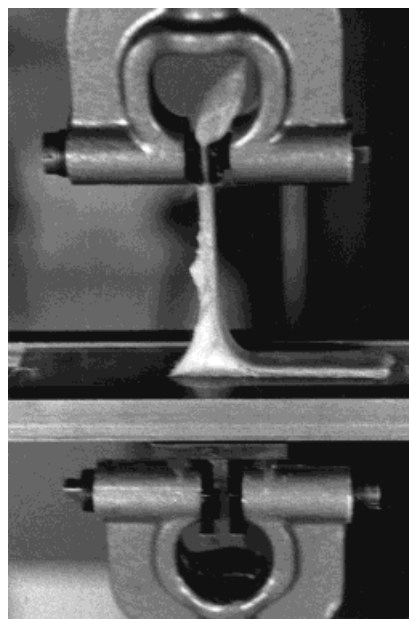

Figure 10 Peeling behavior of the joint containing curing agent at 130°C temperature.
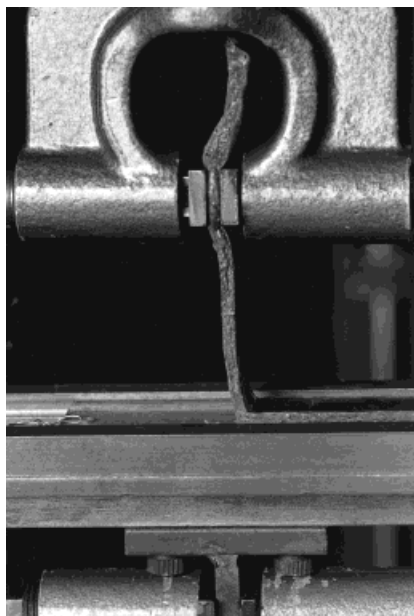
Figure 11 Peeling behavior of the joint containing curing agent at 180°C temperature.

creased the cohesive strength of the rubber, as is expected (Figs. 1 and 2), changing both peel adhesion and peeling behavior of the laminate. Greater energy is dissipated through the viscoelastic deformation of rubber near the peel front during the separation. This is shown in Figures 9–11, where the peeling behavior of joints under different conditions is portrayed. Figure 9 is a control joint, with no crosslinking agent and shows that fibrillar strands of adhesive form during peeling (reflecting the viscoelastic nature of the elastomer). The low viscosity of the rubber leads to low peel strength in the control. When the system is cured *in situ* at 130°C (Fig. 10), substantial deformation around the peel front is observed during separation, reflecting enhanced adhesive strength and toughness, and this contributes to better peel adhesion properties.

At a molecular level, the network structure of the crosslinked rubber is also important. Gent and Tobias[19] previously indicated that the fracture toughness of an elastomer is several magnitudes higher that the theoretical value of a C—C covalent bond (i.e., 100 J m^{-2}, compared with 2–5 J m^{-2}). Lake and Thomas[20] suggested that the high fracture toughness is due to the polymeric nature of the molecular chains comprising the network (i.e., many bonds must be stressed to break one bond). Therefore, at an optimum cross-

link density, the strength is increased, while retaining substantial ductility. Associated toughness is retained.

Further crosslinking at higher curing temperatures (≥ 140°C) has a different effect on adhesion. At these higher crosslink densities (i.e., $\nu > 2.17 \times 10^{-3}$), peel strength decreased and the mode of separation also changes. We propose two possible explanations for this effect. The first is based on the viscoelastic behavior of the elastomer, which predicts that higher crosslink densities promote a more elastic response. With the highly crosslinked elastomers, stresses become more concentrated at the peel front, and this tends to decrease the measured peel strength [as shown in Fig. 11 for a joint wherein the curing temperature is high (180°C)]. Deformation is barely observable, reflecting poor adhesion between PMMA and the elastomer.

A second explanation is at a molecular level. Because the curing was performed *in situ,* it is believed that two competing processes exist: interdiffusion and crosslinking.

Crosslinking rate and the crosslinking density increase linearly with temperature. At high temperatures (150–180°C), the curing rate is rapid, being essentially complete after 30 min. The network structure of the crosslinked rubber is fully developed, and this affects the interdiffusion of chain segments. Crosslinking points create topological constraints, in accordance with the reptation model introduced by de Gennes.[21] The crosslinks of polymer network can be treated as fixed obstacles with respect to the diffusion chain of segments. These limit movement of any single chain (i.e., they cannot move across these points),
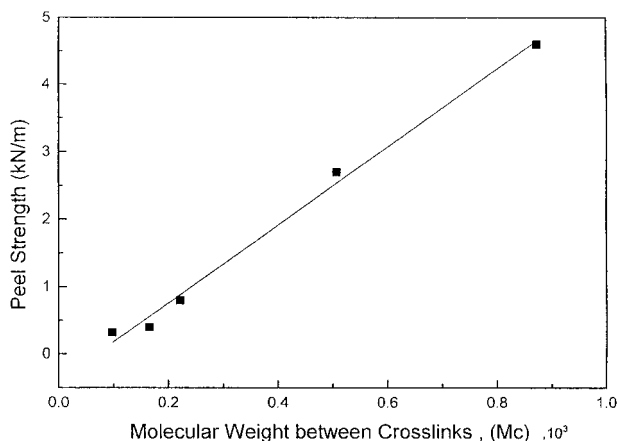

Figure 12 Plot of peel strength P against molecular weight between crosslinks (Mc) of acrylic elastomer.

but tend to move in a snake-like fashion. Thus, the diffusion of chain segments across the interface is slow. Second, the network structure of the crosslinked rubber itself reduces the length of the freely coiling chain segment. This restricts the mobility of chain segments. These factors lead to lower adhesion, compared with the control.

Peel strength can be correlated with crosslink density (ν) or molecular weight between crosslinks, $M_c(Mc = d/\nu)$. The earlier relationship between fracture strength of elastomer and crosslink density is given as[22]:

$$G_c = kM_c^x \qquad (3)$$

with a value of $x \sim 0.5$. This predicts that lower crosslink densities will produce stronger bond strengths. Equation 3, relating fracture strength and crosslink density for a crosslinked elastomer, is developed around the net and noncancelling effect of two factors: the role of crosslink density on numbers of bonds stressed before fracture and the increasing numbers of chains per unit area as the chain length between crosslinks decreases. As Ahagon and Gent have shown,[23] further arrangement to relate fracture energy G_c to M_c needs to allow for chain ends. The role of chain ends is significant for both cohesive tearing in cured elastomers and is equally important in peel strength of laminates. Clearly, elastomer chains that have scarcely penetrated the second polymer (in our case PMMA) are unlikely to contribute to peel strength in the same way as chains deeply immersed in the second substrate.

When peel strength P is plotted as a function of M_c, a straight line (linear regression $R = 0.99$) is obtained (Fig. 12), confirming a relation of the type given in eq. (4):

$$P = kM_c. \qquad (4)$$

The limiting value of M_c for zero peel strength corresponds to ~ 70. The slope of the line is low, reflecting the soft and tacky nature of the acrylic rubber.

These results show that peel strength reaches an optimum when the system is partially crosslinked (i.e., corresponding to low cure temperatures, $<140°C$). Our results are consistent with Zosel's[4] concept (i.e., there is an optimum level of crosslinking for adhesive performance).

CONCLUSIONS

We have shown that *in situ* crosslinking of a soft acrylic elastomer during bond formation can be an efficient method to achieve good peel adhesion. However, the cross-link density should be low, because a higher degree of crosslinking changes the mechanism of adhesion, leading to lower peel strength. For the soap/sulfur curing system, a low crosslink density can be maintained through control temperature, as well as amount of crosslinking agent.

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